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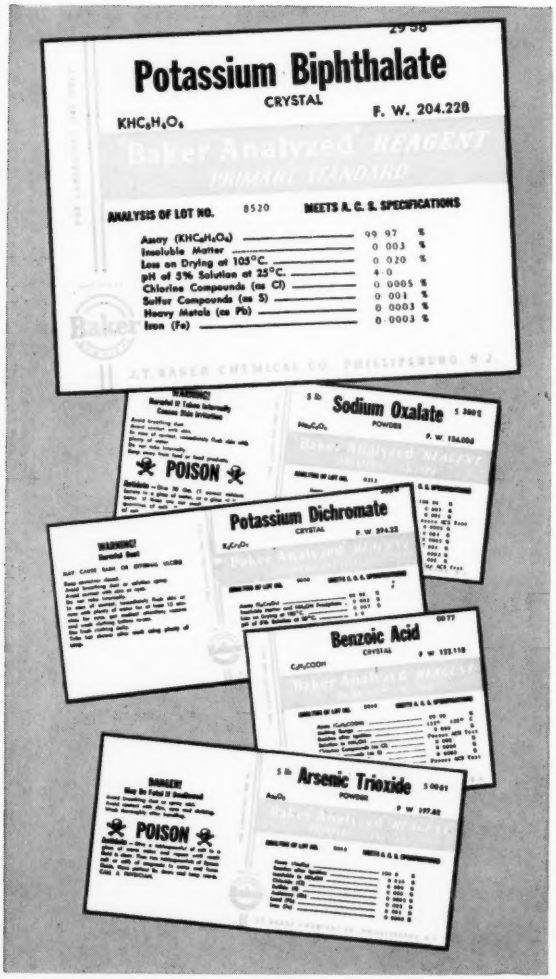
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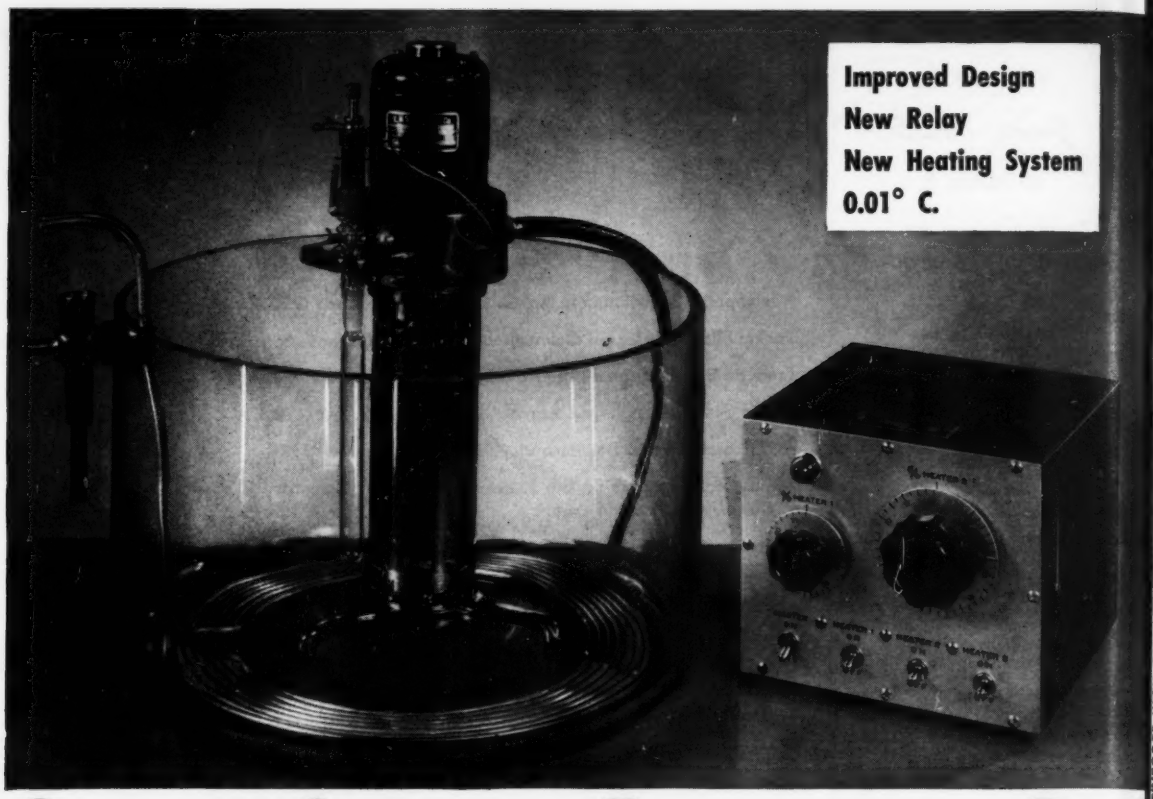

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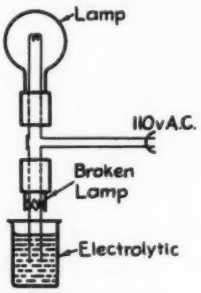
6. IONIZATION

A. ELECTRICAL EVIDENCE

*6-1 *Conductivity.* Board on which is mounted six wide-mouth 100 ml. bottles; each bottle has a rubber stopper in which is inserted a pair of electrodes wired to a socket holding a Christmas tree light bulb; the sockets are wired together in parallel to carry 110-volts A.C., so that only the bulbs of those bottles containing electrically conducting solutions will light up. The first three bottles contain $CuSO_4$-aq., $NiCl_2$-aq., and $K_2Cr_2O_4$-aq.; the last three contain HCl-in-toluene, ethyl alcohol, sugar-aq. **Plug in; show the salt solutions alone conduct.**

6-2 See Figure 6-2. Fasten two light sockets back to back, rewiring them so that they are in series, with a single 110-volt A.C. plug. Into one socket screw a 75-watt bulb; into the other screw a bulb which has been broken, the glass and the filament



CONDUCTIVITY

Figure 6-2

thrown away, so that only the socket and two stout wires to act as electrodes, remain. NaCl; solutions containing Ni^{++}, Co^{++}, Cu^{++}, $Cr_2O_7^{--}$, NaCl, HCl-aq., HCl in toluene, sugar-aq., ethyl alcohol and CCl_4. **Show which solutions conduct. Show pure water does not conduct, but does when a pinch of salt is added.**

6-3 *Electroplating.* $CuSO_4$-aq., two large electrodes such as 2 x 4″ Pt foil fastened to binding posts on a wooden cover provided with a lamp bulb in series, which glows when the electrodes are immersed in a conducting solution, using twenty volts. **Immerse electrodes in $CuSO_4$, showing copper plating out. Reverse poles and show plating direction is reversed.**

6-4 *Electrolysis.* Recall 4-18, electrolysis of KI. Also 1-4, electrolysis of water.

6-5 *Migration of ions.* $BaCl_2$-aq. Half-fill a U-tube with 5% agar-aq. containing $CuSO_4$. When gelled, dust a 2mm layer of charcoal upon each surface, then fill limbs with KNO_3-aq. Immerse U-tube in ice-water. Pass 110-volts D.C. through a 50-watt lamp and through the agar. After half an hour, migration of the blue Cu^{++} can be seen. **Show migration of the SO_4^{--} by adding $BaCl_2$-aq. to the positive limb.**

B. MISCELLANEOUS EVIDENCE

6-6 *Rapid reaction.* $HgBr_2$, KI, $HgBr_2$-aq., KI-aq., mortar and pestle, test tube. **Grind dry powders: slowly forms orange HgI_2. Mix solutions: instantly forms orange HgI_2.**

6-7 Mg ribbon, dil. HCl-aq., HCl in toluene, 2 test tubes. **Show H_2 from aqueous HCl but not from HCl in toluene.**

6-8 *Color of ions.* Anhydrous $CuSO_4$, $CuBr_2$, $CuCl_2$, 3 test tubes. **Show blue Cu^{++} forms upon adding water to the white, brown and green solids.**

6-9 $CoCl_2$, KCNS, dry test tube, ether, $AgNO_3$-aq. **Shake solids, forming blue $CoCl_2$-KCNS complex which remains blue upon shaking with ether. Add water, and pink aqueous layer containing Co^{++} forms. Add drops of Ag^+ to form patriotic colors.**

Turn the page for additional demonstrations

***Footnotes**

6-1 Label the three conducting solutions INORGANIC and the non-conducting solutions ORGANIC. Keep this apparatus to use repeatedly.

6-14 This is a time-consuming but rewarding experiment. Do not perform it hurriedly or the student will miss the details of what is occurring.

Labels for Topic 6. (For code, see instructions for assembling kits, J. Chem. Educ., **32**, 12A(1955).) 6-2-*w*-NaCl, 6-2-*w*-$NiCl_2$ aq., 6-2-*w*-$CoCl_2$ aq., 6-2-*w*-$CuCl_2$ aq., 6-2-*w*-$K_2Cr_2O_7$ aq., 6-2-*w*-HCl aq., 6-2-*w*-NaCl aq., 6-2-*w*-HCl in toluene, 6-2-*w*-sugar aq., 6-2-*w*-ethyl alcohol, 6-2-*w*-CCl_4, 6-3-*N*-$CuSO_4$ aq., 6-4-*w*-KI, 6-4-*w*-NaCl, 6-5-*d*-$BaCl_2$ aq., 6-5-*N*-$CuSO_4$ aq., 6-5-*w*-charcoal, 6-5-*w*-agar, 6-5-*N*-KNO_3 aq., 6-6-*w*-$HgBr_2$, 6-6-*w*-KI, 6-6-*N*-$HgBr_2$ aq., 6-6-*N*-KI aq., 6-7-*w*-Mg ribbon, 6-7-*N*-HCl aq., 6-7-*N*-HCl in toluene, 6-8-*w*-$CuSO_4$ anhydrous, 6-8-*w*-$CuBr_2$, 6-8-*w*-$CuCl_2$, 6-9-*w*-$CoCl_2$, 6-9-*w*-KCNS, 6-9-*N*-ether, 6-9-*d*-$AgNO_3$ aq., 6-10-*N*-NaOH aq., 6-10-*N*-KOH aq., 6-10-*N*-NH_4OH, 6-10-*N*-HCl aq., 6-10-*N*-HNO_3 aq., 6-10-*N*-H_2SO_4 aq., 6-10-*d*-phenolphthalein solution, 6-10-*J*-litmus paper, 6-11-*J*-$BaCl_2$, 6-11-*J*-$Al_2(SO_4)_3$, 6-12-*N*-methylene blue aq., 6-13-*N*-vinegar, 6-13-*N*-HCl aq., 6-13-*w*-Mg ribbon, 6-14-*N*-2 normal H_2SO_4, 6-14-*N*-0.1*N* $Ba(OH)_2$, 6-14-*d*-phenolphthalein indicator, 6-15-*d*-$AgNO_3$ aq. 6-15-*d*-AgOAc aq., 6-15-*d*-$AgNO_3$ aq., 6-15-*d*-NaCl aq., 6-15-*d*-KCl aq., 6-15-*d*-NaCl aq., 6-16-*J*-iron bar, 6-16-*N*-$CuSO_4$ aq., 6-16-*N*-$AgNO_3$ aq., 6-16-*w*-Hg, 6-16-*J*-Zn rod, 6-16-*N*-$Pb(OAc)_2$ aq., 6-16-*J*-chamois bag, 6-17-*d*-$AgNO_3$ aq., 6-17-*d*-HCl aq., 6-17-*N*-KI aq., 6-17-*N*-$HgBr_2$.

6-10 *Indicator colors.* NaOH-aq., KOH-aq., NH_4OH, HCl-aq., H_2SO_4-aq., HNO_3-aq.; phenolphthalein indicator, six pieces of litmus paper fastened to a 10-inch glass rod. **Repeat 4-13, showing litmus turns blue with OH^- and pink with H^+. Show few drops of phenolphthalein indicator in each turns red with OH^-, colorless with H^+.**

C. COLLIGATIVE EVIDENCE

6-11 *Freezing point apparatus. Boiling point apparatus.* Ring stand with four rings containing bag of sugar at height 1, bag of salt at height 2, $BaCl_2$ at height 3, and $Al_2(SO_4)_3$ at height 5. **Illustrate relative depression of F.P. or elevation of B.P. due to ionization.**

6-12 *Osmotic pressure.* Methylene blue-aq. in semi-permeable thimble immersed in a 400 ml. beaker of water; a 3-ft. capillary tubing sealed to and projecting upwards from the thimble. **Start osmosis a week before lecture, following its rise from day to day.**

D. APPARENT DEGREE OF IONIZATION

6-13 Vinegar, HCl-aq., Mg ribbon, 2 test tubes, conductivity apparatus 6-2. **Show relative conductivities by the brightness of the light with vinegar and HCl, and compare with their relative rates of reaction with Mg.**

E. SOME IONIC REACTIONS

*6-14 See Figure 6-14. Burette containing 2 normal H_2SO_4, phenolphthalein solution, 400 ml. beaker containing 200 ml. of 0.1 N $Ba(OH)_2$; electrodes connected in series with a milliammeter and a 6-volt source. **Add a few drops of phenolphthalein indicator to the $Ba(OH)_2$ solution; solution turns red due to excess OH^-. Now run in H_2SO_4 from the burette; white $BaSO_4$ precipitates, but the solution still conducts and remains red due to excess OH^-. When an amount of acid equivalent to the OH^- has been added, conductivity ceases. Any additional acid turns the phenolphthalein colorless, but conductivity again increases due to H^+ and SO_4^{--}.**

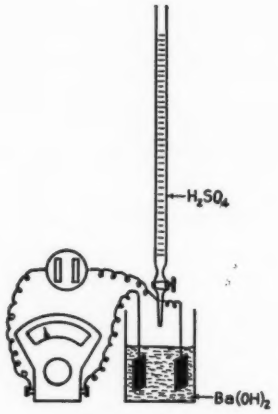


Figure 6-14

6-15 Six test glasses, $AgNO_3$-aq., AgOAc-aq., unknown solution (Ag^+), NaCl-aq., KCl-aq., unknown solution (Cl^-). **Show how the contents of each solution can be detected by the chemical reactions of its ions.**

6-16 *Displacement.* Repeat 1-12, 1-13, 1-14, and 1-15 and explain in terms of ionic equations.

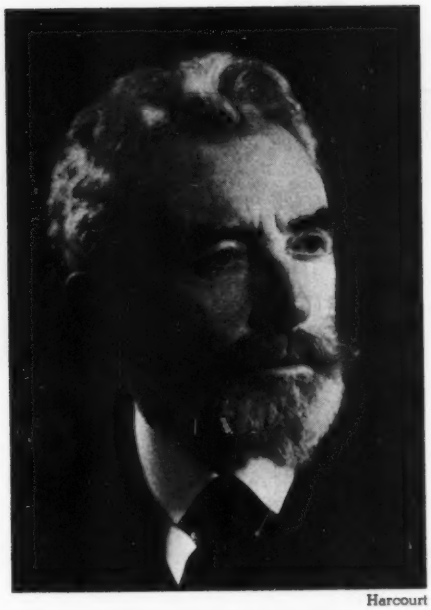
6-17 *Double decomposition.* Repeat 1-16 and 1-17, and explain in terms of ionic equations.

F. COMMON ION EFFECT. SOLUBILITY PRODUCT.—See topic 8, Equilibrium.

Next month's Tested Demonstrations in General Chemistry

7. ENERGY

For a complete list of topics for 1955–6 see J. Chem. Educ., 32, 28–9(1955)



Harcourt

Frédéric Swarts

(See page 301)

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Editor's Outlook

I RECENTLY had occasion to participate in a panel conference on the training of science teachers. I suspected that it would be dominated by "educationists" since most of the members of the panel came from the teacher's colleges. The results were not so bad as I had feared. The contrast in the points of view of "education" and the "subject-matter fields" is often exaggerated. To be sure, the discussion frequently turned to technical details rather than broad generalities, but after all, the practical question before the house does seem to be: How shall the curriculum for the prospective science teacher be divided among subject matter, general education, and professional subjects ("education")?

The views expressed in the discussion of this question were not as extreme as might be supposed. The belief that "you don't have to know *what* to teach, but only *how* to teach it" is not common among educationists, no matter what people may tell you. No member of this panel, and only one voluble member of the surrounding audience, seemed to hold this opinion. We must be equally careful not to take the opposite extreme view: that if you know enough chemistry, for instance, you will certainly be a good teacher. We must be ready to admit that teaching is a profession—we chemists are jealous enough of our own professional standing. The professional, in any field, has need of a good deal of breadth in his training. For instance, he must have an intimate knowledge of the raw material with which he works; and the chemistry teacher's raw material is human, not chemical.

I was impressed with the idea that there is no good reason for the feud which seems to go on between many of us and the people who are trying to train our teachers and administer our schools. We imply (perhaps really *believe*) that we could do the job better than they. Is this because we do not think they are good enough, because they do not have the right objectives, or what? They think we are too narrow and do not see the broader implications of educational problems. We think they are misled by false doctrines. What we really need is more opportunities to get together and try to see each others' viewpoints. Some compromises will probably have to be made on both sides.

If we chemists really want to do something about chemistry teaching in the high schools we should cooperate with such organizations as the National Science Teachers Association, where secondary-school problems are seen in their broader perspective. We cannot "go it alone." At the high-school level the real thing to worry about is not the teaching of chemistry but of science in general. Chemistry at this level is only part of a larger pattern.

We certainly have some important ideas to contribute to this problem of science teaching. We should get together with the other people who are concerned with other parts of it. Our combined efforts should accomplish something.

THE article by Karol J. Mysels, on page 319, is the second of a series. The subject is one which may call forth a good deal of comment. With the rapid advance of chemical science it is inevitable that textbooks fall behind. However, the object of these articles is not to point out the obvious fact that textbooks become obsolete but to call to attention the altogether too common instances of errors and mistaken conceptions which were not corrected when they should have been and by oversight have been perpetuated in the process of transfer from one book to another.

Dr. Mysels welcomes correspondence on this matter and has been warned that critics will doubtless attack his choice of "errors." Indeed, we hope for a great deal of controversy. Honest differences of opinion will of course develop, which after all are the fuel that turns the wheels of scientific progress. We hope that this series will continue for a long time, perhaps intermittently and contributed from many sources.

NUCLEOPHILIC SUBSTITUTION IN AROMATIC SYSTEMS

RICHARD G. GILLIS
Royal Melbourne Technical College, Victoria, Australia

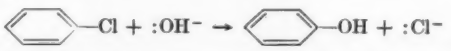
AROMATIC nucleophilic substitutions have not had nearly as much attention as they deserve in comparison with electrophilic substitutions in aromatic systems, and with both kinds of substitution in aliphatic compounds. Now that undergraduates are more generally being taught something of structure and electronic mechanisms, it seems worth while to classify and summarize those important aromatic nucleophilic reactions with which they should become acquainted, placing emphasis on those of special importance in general laboratory practice and in commercial operations. Such a summary is attempted in this review, without going deeply into details of mechanism. For these, and for further examples, reference should be made to the extensive report of Bunnett and Zahler (*1*) and the critical discussion by Ingold (*2*).

We shall define aromatic nucleophilic substitutions as those reactions in which a Lewis base (nucleophile, electrodotic reagent) replaces hydrogen or some other group directly attached to an aromatic system, with or without rearrangement.[1] In general these reactions may be formulated thus:

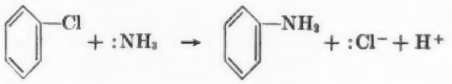
the nucleophile :N attacking the ring at a point of electron deficiency. Substituents which accentuate this deficiency will in general facilitate the reaction. The normal rules for electrophilic substitution such as the Hammick-Illingworth rule are reversed, and powerful activation in the para and ortho positions is caused by -onium groups (especially diazonium), nitro, nitroso, cyano, carboxyl, carbonyl, and sulfone groups in particular. However, there are cases of nucleophilic substitution without the help of such activating groups, and also some anomalous orientations. Mostly these reactions are of the S_N2 type (bimolecular) but some are almost certainly S_N1 (unimolecular); others have cyclic intermediates but can still be classed as nucleophilic. The main types are here arranged into six categories, according to the group replaced. This has been found a suitable approach in undergraduate teaching.

[1] The entire aromatic ring is taken as the origin or focus of attention rather than some particular atom. One might equally well say that the ring makes an electrophilic attack on the Lewis base, but unless a convention is adopted and adhered to, confusion will result. Brown and co-workers have recently used the opposite point of view in classifying the Friedel-Crafts reaction as a nucleophilic substitution (*3*).

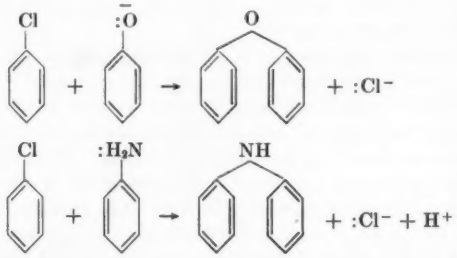
Replacement of Groups Normally Stable as Anions, Without Activation of the Ring. Some important commercial reactions fall into this class: One is the Dow process for the manufacture of phenol from chlorobenzene (*4*):



Another is the related ammonolysis of chlorobenzene to aniline (*5*):

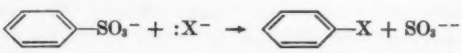


The formation of diphenyl oxide and diphenylamine as by-products is strong evidence for the mechanism. They can be seen to be the result of a second stage of the same process.



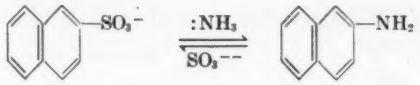
The formation of aniline from phenol has been the subject of patent application (*6*), as has the formation of diphenylamine from phenol and aniline (*7*). These reactions all require high temperatures to give useful yields (200–400°C.); the same type of reaction can be carried out at much lower temperatures when suitable activating substituents are present.

Also requiring severe experimental conditions are the reactions of aromatic sulfonates in fusions, *e. g.*, the formation of sodium phenate from sodium benzenesulfonate and sodium hydroxide.

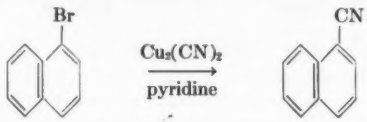


In this subclass, X may be OH, SH, CN, and NH_2, and important examples exist in the naphthalene and anthraquinone as well as the benzene series.

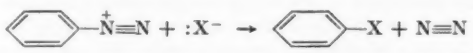
The Bucherer reaction (*8*) is a nucleophilic substitution in which activation by substituents is not essential:



and so too is the Rosenmund-von Braun reaction (*9*):

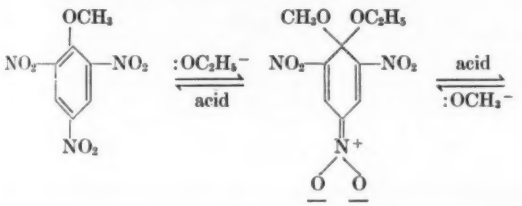


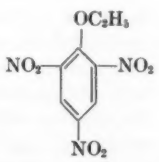
The replacement of the diazonium group by halogen, as in Sandmeyer-type reactions, is a nucleophilic substitution and can proceed without activation of the ring by substituents, though a catalyst (usually copper) is often desirable. This reaction can be formulated generally as:



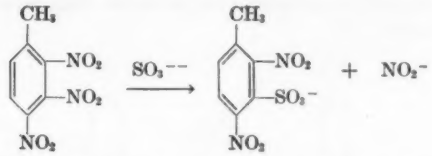
and X may be OH, OR, F, Cl, Br, I, CN, and NO_2 in particular. This reaction is included here for convenience, although nitrogen is a neutral molecule and not an anion; its great stability provides much of the driving force of the reaction.

Replacement of Groups Normally Stable as Anions with Activation of the Ring. Historically the most important reaction in this class is the reversible interconversion of 2,4,6-trinitroanisole and 2,4,6-trinitrophenetole discovered by Meisenheimer (*10*), who isolated the intermediate complex as the sodium salt.

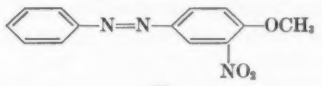




The activation of the chlorine by the two nitro groups in 2,4-dinitrochlorobenzene is well known, and its use as a starting material for 2,4-dinitrophenol and 2,4-dinitrophenylhydrazine should require no elaboration. Related important applications are the use of 2,4-dinitrochlorobenzene in the characterization of amines, mercaptans, and phenols (*11*) and the use of 2,4-dinitrofluorobenzene in the identification of amino end groups in peptides (*12*). A single nitro group can produce similar activation for the nucleophilic replacement of halogen as in *o*- and *p*-nitrochlorobenzene. Activation of one nitro group by another is the basis of the purification of 2,4,6-trinitrotoluene by the removal of unstable isomers with sulfite as soluble sulfonates. The nitro group replaced is that meta to the methyl group (*13*).

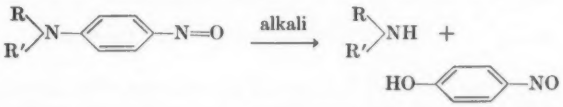


An interesting example of activation due to a combination of groups is the observation by Galmarini (*14*) that 3-nitro-4-methoxyazobenzene (I) will transetherify under conditions which do not cause exchange in 4-methoxyazobenzene or *o*-nitroanisole separately.



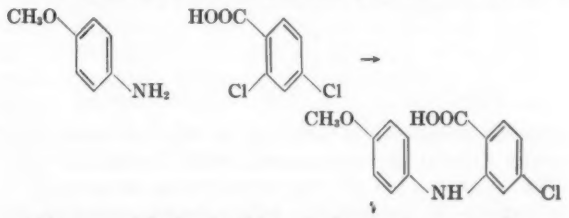
(I)

Activation by the nitroso group has been recognized for many years and is the basis of the older synthesis of secondary aliphatic amines. The apparent anomaly



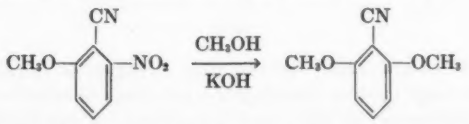
that nitrosobenzene is brominated (electrophilic substitution) in the para position has been resolved. This reaction occurs only in the presence of hydrobromic acid (*15*) and the nitroso group is not truly para-ortho directing for electrophilic substitutions.

Activation by the carboxyl group enables ortho halogenated benzoic acids to undergo such reactions as that illustrated, a key step in the synthesis of Atebrin.



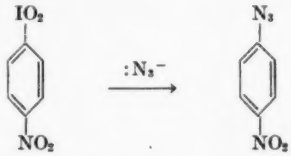
The para chlorine in this case does not react and copper is a necessary catalyst. It appears from recent work that a cyclic intermediate occurs (*16*) which explains adequately the attack at the ortho halogen only.

An example of activation by the cyano group is the formation of 2,6-dimethoxybenzonitrile from 2-nitro-6-methoxybenzonitrile in 70 per cent yield (*17*).

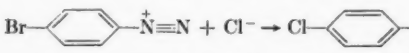


In accordance with its known meta directing power

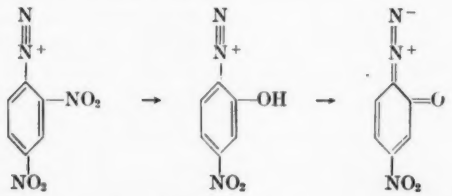
in electrophilic substitution, the iodoxy group should be para activating for nucleophilic substitution; however, *p*-nitroiodoxybenzene with azide ion has been shown to give *p*-nitrophenylazide rather than *p*-iodoxyphenylazide (*18*).



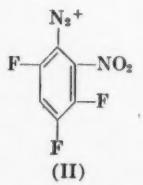
A positive pole directly attached to an aromatic ring is powerfully deactivating and meta directing for electrophilic substitution. It should be para-ortho activating for nucleophilic substitutions and such is the case, the most important example being the diazonium ion. Electrophilic substitution is rarely observed in aromatic diazonium ions since the deactivation of the ring requires experimental conditions which are usually too severe for the relatively unstable ion to survive. However, nucleophilic substitutions, both para and ortho, do occur. Reactions of the type:



have been observed and should be anticipated as a possible cause of embarrassment in preparative work; their scope is summarized by Saunders (*19*). Replacement of an ortho substituent also is not uncommon, especially by hydroxyl, as further loss of a proton gives the very stable diazo oxide.

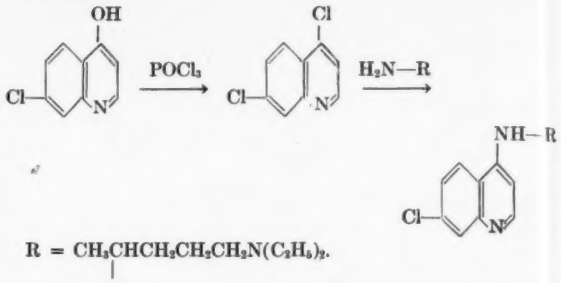


Several summaries of this type of reaction have been made without the mechanism's being recognized (*20*). The diazonium ion (II) has recently been shown to give a variety of nucleophilic substitutions according to conditions (*21*).



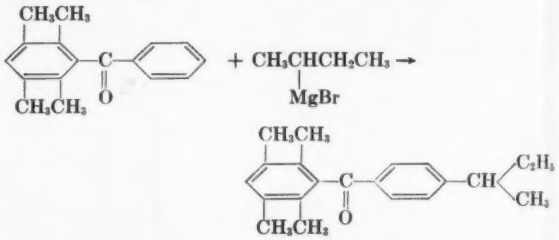
(II)

The deactivation by the ring nitrogen of pyridine-type rings toward electrophilic reactions is reflected in the activation of the α and γ positions for nucleophilic substitutions. Many of these take place in an acidic environment so that the pyridinium ion is the effective activator. Adequate examples are found in the synthesis of Chloroquin, Atebrin, and similarly constituted antimalarials.

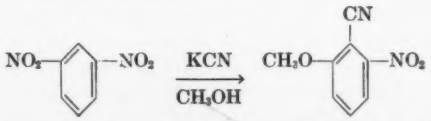


Replacement of Hydrogen Which Appears as Hydride Ion. Since hydride ion is stable only in nonaqueous media, examples of reactions in this class are less common than in the first two classes. The most important is the Chichibabin reaction (*22*), the amination of heterocycles with alkali amides. In pyridine the orientation is unusual, though not anomalous: the α position is preferred to γ and further substitution occurs at α' giving 2,6-diaminopyridine.

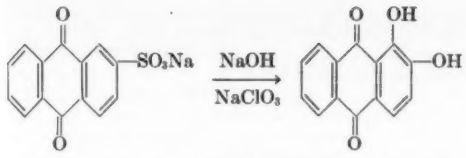
A very unusual case in which activation is by the carbonyl group is that reported by Fuson and Tull (*23*); steric effects from the duryl group may be important in this example.



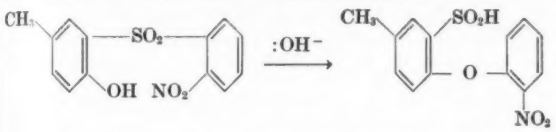
Replacement of Hydrogen as Hydride Ion Followed by Oxidation to Proton. Hydrogen may be replaced by a nucleophile in aqueous media if the hydride ion can be immediately oxidized. Suitable mild oxidants have been atmospheric oxygen or potassium ferricyanide in the alkaline conversion of *m*-dinitrobenzene to 2,4-dinitrophenol, and of *sym.*-trinitrobenzene to picric acid. Similarly, trinitrobenzene can be converted to picramide by hydroxylamine which acts as its own oxidizing agent (*24*). An apparently related reaction is the conversion of *m*-dinitrobenzene to 2-nitro-6-methoxybenzonitrile by the action of potassium cyanide in methanol (*17*). Since the yield is low (22 per cent) the mechanism may not be clearcut.



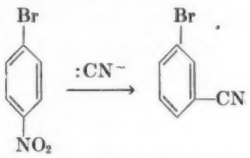
An example from an important dyestuff synthesis is the oxidative alkali fusion of anthraquinone-2-sulfonic acid leading to alizarin.



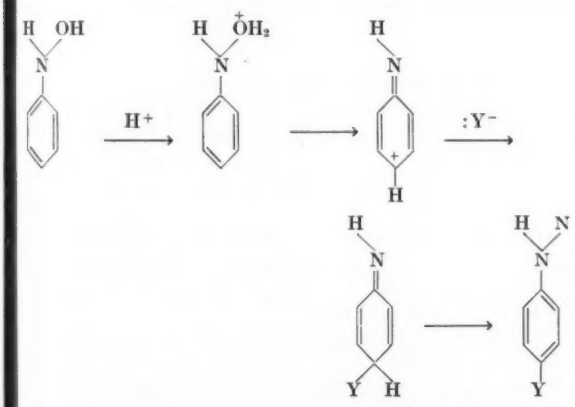
Nucleophilic Substitution Accompanied by Rearrangement. Two fairly well known rearrangements which are essentially nucleophilic substitutions are the Smiles rearrangement (*25*) of which the following is an example:



and the von Richter reaction (*26*) which is illustrated by a simple typical case:

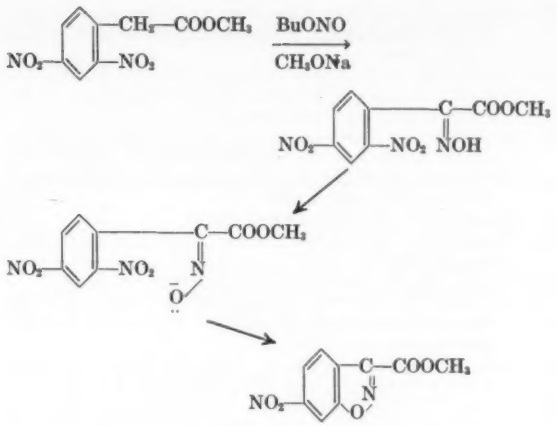


The rearrangement of phenylhydroxylamine to *p*-aminophenol has recently been recognized as an intermolecular nucleophilic substitution rather than a simple intramolecular rearrangement by Heller, Hughes, and Ingold (*27*), who suggest that the course of the reaction is:



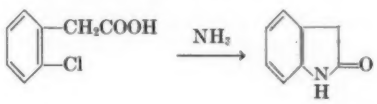
where Y is OH or any other available nucleophile; in alcoholic media O-ethers are observed as products.

Nucleophilic Substitution Leading to Ring Closure. Most ring closure reactions occur under acidic conditions and follow an electrophilic course, *e. g.*, the formation of anthraquinone from O-benzoylbenzoic acid. There are, however, at least two ring closures involving a nucleophilic step, and possibly others have been recorded but are so far unrecognized. The first is the formation of benzisoxazoles in such a reaction sequence as that shown, which was used by McGhie and co-workers (*28*) in a synthesis of *p*-aminosalicylic acid.



Another example of the same reaction is that 2,4-dinitrophenylacetone under similar conditions gives 3-acetyl-6-nitrobenzisoxazole (*29*).

A second type of nucleophilic ring closure is the synthesis of oxindole recently reported by Neill (*30*). Al-



though it is not yet clear what are the intermediate stages, one must be nucleophilic. A similar closure leading to a six-membered ring (3,4-dihydrocarbostyril) has also been reported (*31*).

Addendum. As was mentioned in the introduction, it is not the purpose of this survey to discuss mechanisms in detail. This is adequately done elsewhere. But for those whose interest will lead them to seek recent kinetic studies, the postwar papers of Berliner (*32*), Bevan (*33*), Miller (*34*), and Sandin (*35*) will provide useful material. Miller has also published a comprehensive summary of the activation to be expected from various groups in terms of their inductive, mesomeric, and electromeric effects (*36*).

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EDGAR C. PITZER
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Your pocket slide rule may be used for direct conversion from hydrogen-ion activity to pH, or vice versa, without the need for arithmetical computation.

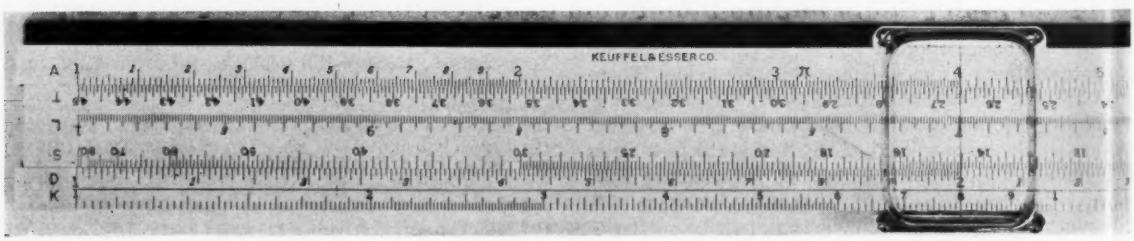
Remove the slide, invert, turn end for end, and align the 1.0 mark on the L scale with 1 on the D scale. A number on the D scale will be aligned with the logarithm of its reciprocal on the L scale, hence the decimal part of a pH value can be read off directly, as shown in the illustration.

For example, determine the pH corresponding to a hydrogen-ion activity of 2×10^{-3}. Set the index to 2 on the D scale, and find the value on the L scale. The corresponding decimal is read as 0.7, approximately. Since the solution is more acid than pH 3, the digit to the left of the decimal point is obviously 2, and therefore the pH is approximately 2.7.

To calculate the hydrogen-ion activity corresponding to pH 4.5, set the slider to 0.5 on the L scale. The reading on the D scale is 3.15. The solution is less acidic than 10^{-4} M, so the hydrogen-ion activity is 3.15×10^{-5} M.

The interconversion of equilibrium constants and pK values is readily accomplished in the same manner. Thus for acetic acid, $K = 1.8 \times 10^{-5}$, and pK is found to be 4.74, approximately.

Slide rules containing the CI scale on the same face as the log scale obviously do not require the inversion of the sliding scale. Simply set the index on the CI scale and read the corresponding decimal on the L scale.



FRÉDÉRIC SWARTS: PIONEER IN ORGANIC FLUORINE CHEMISTRY

GEORGE B. KAUFFMAN
University of Florida, Gainesville, Florida

WHEN in a reminiscent mood, Frédéric Swarts loved to tell his colleagues how he had swallowed a few cubic centimeters of difluoroethyl alcohol in order to prove the physiological inertness of this compound. This substance was only one of scores of organic fluorine compounds which Swarts was first to prepare and study with his characteristic thoroughness—compounds through which he became internationally recognized as a pioneer in this field of research.

The practical results which, within the last decade, have come of Swarts' brilliant theoretical work, would no doubt have astonished him. He established a basic far-reaching body of knowledge which ultimately has made possible multimillion-dollar industries supplying heat- and chemical-resistant materials for use as lubricants, refrigerants, heat-transfer media, plastics, and coatings, to mention only a few of the applications (*1*).

LIFE

Frédéric Jean Edmond Swarts was born at Ixelles, a suburb of Brussels, on September 2, 1866, at which time his father Théodore was assistant to Kekulé (*2*) at the University of Ghent. Following in the footsteps of his illustrious father, who had succeeded Kekulé in 1867, young Swarts entered the University of Ghent in 1883 as a student in the École normale des Sciences. When he was nineteen he was made *préparateur adjoint* to his father in the general chemistry laboratory. In 1889 he received the degree of *Docteur en chimie* and, two years later, that of *Docteur en médecine*. He then began his professional career as *répétiteur* at the Écoles speciales du Génie civil et des Arts et Manufactures.

In 1901 Swarts took charge of the general chemistry course for the engineering students, and two years later he was further intrusted with teaching the course for the general chemistry degree of the Faculté des Sciences, a post which became vacant upon the retirement of his father. Thus, Frédéric Swarts came to occupy the very position which had been made so famous forty years before by Kekulé. Finally, in 1910, he was asked to direct the chemistry laboratory of the doctoral candidates.

He continued to pursue his teaching career at Ghent until his retirement in 1935. After this, he still continued to work in his personal laboratory until a few months before his death. He died at Ghent on September 6, 1940, as a result of a chronic lung infection which, because of the German occupation, he had not been able to remedy, as he had previously done, by residence in a milder climate.

A list of the honors bestowed upon Frédéric Swarts is long and impressive indeed. For his first monograph, "Contribution à l'étude des combinaisons organiques du fluor" (1900), the Académie Royale de Belgique awarded him its Médaille d'Or. In 1902 he became corresponding member of the Classe des Sciences of that institution, and in 1911, titular member. In 1919 the Belgian government awarded him the Decennial Prize in the Physical and Chemical Sciences.

As his work progressed, it was recognized by institutions outside his own country. He became corresponding member of the Institut de France and the Academy of Madrid; doctor *honoris causa* of the Universities of Brussels, Cambridge, and Nancy; honorary member of the Royal Institution of Great Britain; member of the Institut International de Chimie Solvay and its president after Sir William Pope; and charter member of the International Union of Pure and Applied Chemistry and later its vice-president. The governments of Belgium and France elected him Grand Officer of the Ordre de la Couronne, Commander in the Order of Leopold, and Officer in the Legion of Honor (*3*).

The volume of Frédéric Swarts' work prohibits its detailed discussion here, permitting only a brief glance at the more important highlights.

SYNTHESES

In the field of organic fluorine chemistry Swarts was a true pioneer. To be sure, previous to his efforts, Dumas and Peligot (*4*), Fremy (*5*), and especially Moissan (*6*) had isolated a few organic fluorine derivatives, but it was not until the advent of Swarts' monumental labors that a direct, concentrated attack was made upon the problem.

The difficulties and obstacles involved would have discouraged any but the most tenacious and ingenious worker. For one thing, HF and F_2 attack glass vessels, so that platinum or other metallic apparatus must be used. For another, reactions of organic materials with fluorine are often violent and difficult to control. Fluorine exhibits a great affinity for carbon and hydrogen. Also, many inorganic fluorinating agents are hygroscopic, and substitution of fluorine in the aliphatic series is greatly hindered by the presence of water vapor; anhydrous HF was rare and difficult to obtain, and its esterifications are much slower than those of the other hydrohalogen acids (*7*); and the reagents used were highly caustic and toxic.

Having rejected direct fluorination as a preparative method, after obtaining poor yields and poor products,

Moissan (*6*), one of Swarts' most important predecessors in this field, had turned to the use of other fluorinating agents. By double decomposition with inorganic fluorides, notably silver fluoride (*8*) and arsenic fluoride (*9*), he had been able to replace halogen atoms on halogenated organic compounds with fluorine atoms.

Swarts' first task was to perfect some indirect fluorination processes. His new method of fluorination ("Swarts reaction," 1892) involved the action of a mixture of bromine and antimony trifluoride upon polyhalides in which the halogen atoms were on the same carbon atom (*10*). In 1896 he began to use mercurous fluoride (*11*), and with its aid he soon isolated many alkyl fluorides (*12*), fluoroacetic acid (*11*), monofluoroethanol (*13*), etc.

As early as 1891 Swarts had synthesized trichlorofluoromethane (*14*), the first of his long list of organic fluorine compounds. He further isolated a large number of chlorofluoro and bromofluoro derivatives of methane (*15*) and ethane (*16*, *17*), together with ethylenic derivatives (*10*). Worthy of note here is the fact that these aliphatic chlorofluoro compounds, as prepared by Midgley and Henne (*18*) by a modified Swarts reaction (1930), were the first fluorochemicals to be used commercially. Under the general name of "Freons," they still comprise the greatest part of all fluorochemical production and are widely employed as refrigerants.

Swarts' method was not without its limitations. By the use of antimony trifluoride on aliphatic compounds, it was not possible to replace with fluorine more than two of the halogen atoms on any one carbon atom ("Swarts' rule"), *i. e.*, aliphatic compounds containing the grouping $-CF_3$ could not be prepared by this method (*16*).

In the aromatic series, however, Swarts readily obtained the grouping $-CF_3$ by the use of antimony trifluoride and succeeded in preparing trifluorotoluic acid. It was only at a much later date, as a result of his increased experience, that Swarts succeeded in preparing aliphatic $-CF_3$ derivatives by an indirect method. From phenyl fluoroform, $C_6H_5CF_3$, he prepared the derivative trifluoro-ortho-toluidine (*19*), which on oxidation gave trifluoroacetic acid, CF_3COOH, the strongest organic acid known (*20*). From this he obtained a whole series of derivatives—trifluoroacetic anhydride, trifluoroacetic ester, trifluoroacetoacetic acid (*21*), etc. The last-named compound is the only β-ketonic acid stable enough to be distilled without decomposition.

By electrolysis of trifluoroacetic acid (*22*), Swarts obtained very pure hexafluoroethane (*23*) and hoped to be able to use this for the determination of the atomic weight of fluorine by Guye's method (*24*).

A whole new series of derivatives became possible when, by the preparation of diazonium intermediates in concentrated HF, Swarts succeeded in introducing the fluorine atom into the aromatic nucleus itself (*25*).

Early in his syntheses (1895) Swarts obtained bromochlorofluoroacetic acid, which proved to be of considerable theoretical interest (*26*). On its neutralization with strychnine, two active salts were obtained. This was the first known example of an optically active compound's containing only two carbon atoms. By loss of CO_2, Swarts should have obtained the active bromochlorofluoromethane, but decarboxylation was accompanied by racemization, and the hydrocarbon obtained was inactive.

Throughout his research career, Swarts also prepared many organic halogen compounds in a highly pure state and carefully determined their properties in order to compare these with the corresponding fluorine derivatives.

CHEMICAL PROPERTIES OF ORGANIC FLUORINE COMPOUNDS

Swarts found that the effect of the presence of fluorine in an organic compound is determined by the competition between two opposing forces: (1) the affinity of fluorine for carbon, and (2) the affinity of fluorine for hydrogen. Therefore, according to the structure of the compound in question, the presence of fluorine may confer either great stability or great instability.

Affinity of Fluorine for Carbon (Confers Stability). The strong affinity of fluorine for carbon makes many of these compounds indifferent to hydrolysis and similar to the corresponding hydrocarbons. Thus, it is often possible to attack other regions of the molecule, while leaving the fluorinated part intact—*e. g.*, the oxidation of trifluoro-ortho-toluidine to trifluoroacetic acid as mentioned above. Similarly, the stability of many fluorine compounds toward metals, water, bases, and heat, and their inertness toward glass can be attributed to the strength of the C—F bond.

As a result of the very intense intramolecular forces caused by the strength of this bond, the intermolecular forces that exist are very weak, and it is this lessened tendency toward association that has often brought up the suggestion that these compounds be used as standards in the study of various physical properties (*27*).

Affinity of Fluorine for Hydrogen (Confers Instability). The affinity of fluorine for hydrogen is shown by the ease of decomposition of secondary alkyl fluorides (*12*), and the hydrogenation of aromatic compounds containing fluorine in the ring (*28*, *29*). Both these types of reaction are accompanied by loss of HF.

PHYSICOCHEMICAL STUDIES OF ORGANIC FLUORINE COMPOUNDS

Thermochemistry. In 1919 Swarts made an exhaustive thermochemical study of more than 60 organic fluorine compounds (*30*). His determinations of their heats of combustion showed that the change in internal energy accompanying the substitution of hydrogen by fluorine was not constant, but increased with the number of atoms of fluorine attached to the same carbon atom. A study of boiling points showed that fluorinated organic compounds are usually more volatile than the corresponding nonfluorinated com-

pounds owing to the increased intramolecular and resultant decreased intermolecular forces.

Refractometry. In 1923 in a refractometric study of organic fluorine compounds (*31*), Swarts showed that the molecular refractions of such compounds were lower than those of the corresponding hydrocarbons, and that the atomic refraction of fluorine was less than that of the other halogens; in fact, less than that of all the other elements including hydrogen.

Viscosity. In 1931 Swarts' study of the viscosities of the same compounds further confirmed the weakness of the intermolecular forces (*32*).

CONCLUSION

As his friend and collaborator, Prof. V. Desreux, has aptly pointed out, the scientific work of Frédéric Swarts constitutes a homogeneous whole, executed with method and precision and following a maturely considered order. All these are qualities which perfectly reflect the character of the man.

Swarts is described as a chemist whose enthusiasm was tempered with rigorous self-discipline. Setting high standards for himself, he demanded equally high standards of others. His criticism was severe and biting, but at the same time remarkably accurate and constructive.

To an outsider Swarts might appear timid, distant, and retiring, but his students and research collaborators learned to revere him for his wide knowledge, his unusual capacity for reflection, his scrupulous conscience, his clear vision, his candor, and his devotion to and faith in science (*3*).

In reviewing the life and work of Frédéric Swarts, one is tempted to draw an analogy between him and his fellow countryman, the composer César Franck. Each devoted himself wholeheartedly to his art; each was a bold innovator and an original thinker; and although each did his life's work in a narrowly circumscribed physical environment, Franck in the organ loft at St. Clothilde, Swarts at the University of Ghent, each is numbered among Belgium's outstanding creative minds.

ACKNOWLEDGMENT

The author wishes to acknowledge the assistance of Prof. V. Desreux of the University of Liège, who provided much valuable material.

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SUMMER CONFERENCE

A chemistry teachers' summer conference will be held on the campus of the University of Rochester from June 27 to 30. The Rochester Section of the American Chemical Society offers a scholarship sufficient to cover the registration fee and the cost of lunches and dinners, to any chemistry teacher in a high school in the Central-Western Zone of the New York State Science Teachers Association.

Applications must be received by June 10, and may be sent to Kodak Park Works, Eastman Kodak Company, Rochester 4, New York.

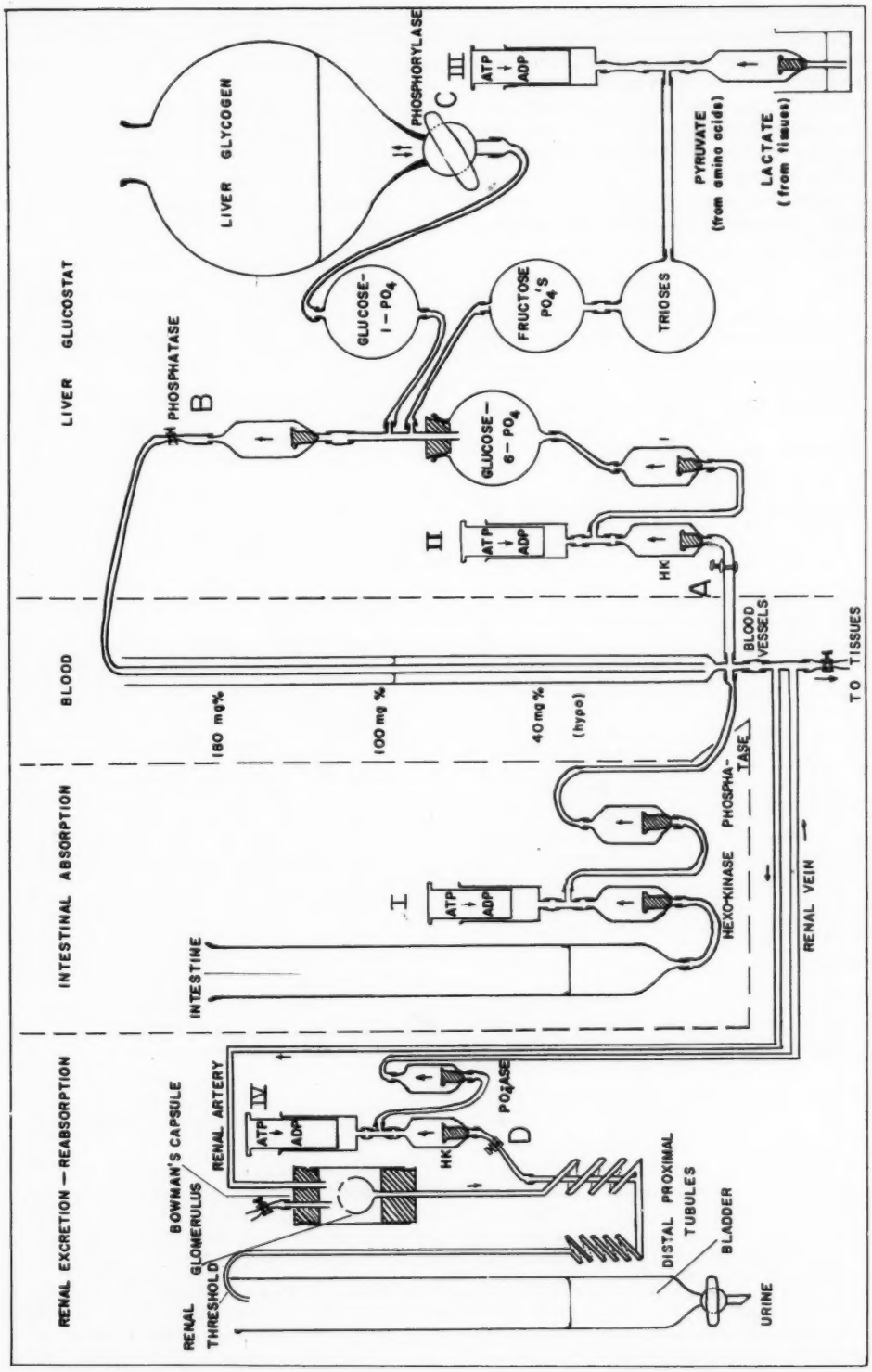
RENAL EXCRETION — REABSORPTION
INTESTINAL ABSORPTION
BLOOD
LIVER GLUCOSTAT
LIVER GLYCOGEN
PHOSPHORYLASE
C
III
ATP
ADP
PYRUVATE
(from amino acids)
LACTATE
(from tissues)
GLUCOSE-1-PO4
FRUCTOSE PO4'S
TRIOSES
PHOSPHATASE
B
GLUCOSE-6-PO4
II
HK
A
BLOOD VESSELS
TO TISSUES
180 mg%
100 mg %
40 mg %
(hypo)
HEXOKINASE
PHOSPHA-TASE
RENAL VEIN
INTESTINE
I
BOWMAN'S CAPSULE
GLOMERULUS
RENAL ARTERY
IV
PO4ASE
D
RENAL THRESHOLD
DISTAL PROXIMAL TUBULES
BLADDER
URINE

Figure 1

MODEL GLUCOSTAT

HARRY J. LOWE
University of Texas, Galveston, Texas

A WORKING model glucostat is described. The apparatus is designed to illustrate the transportation of glucose into and out of cells in the intestine, liver, and kidney. Employing the concepts of mass action, expenditure of high-energy phosphates, irreversible hydrolytic reactions, and hormonal regulation, it is possible to illustrate postabsorptive hyperglycemia, glucose tolerance, renal glycosuria, renal threshold, gluconeogenesis, diabetes, von Gierke's disease, tissue utilization, and numerous other conditions generally discussed under glucose metabolism in biochemical courses.

The model glucostat described has been designed to illustrate and emphasize the mechanisms whereby glucose is transferred across cell membranes against a concentration gradient. The reactions may be depicted as shown by the diagram.[1]

The complete transfer of glucose across the cell involves two exothermic reactions which for all practical purposes may be considered irreversible. This has been achieved in the apparatus by introduction of simply constructed valves to prevent the back flow of fluid (methylene blue solution). (See Figure 1.)[2] The actual appearance of the assembled apparatus is shown in the accompanying photograph (Figure 2).

Intestinal absorption of glucose and postprandial hyperglycemia is demonstrated by a pumping action (expenditure of ATP) at syringe I.[3] The elevated "blood glucose level" drops slowly by hydrostatic pressure to "liver glycogen." The rate is regulated by a screw clamp at *A* representing hexokinase. Closing *A* represents hyperinsulinism or hypoadrenalism.[4] Opening *A* represents hypoinsulinism or hyperadrenalism. The role of ATP in this reaction is to accelerate glycogenesis and hypoglycemia results when rate of pumping at syringe II exceeds the rate at which the fluid is siphoned back into the blood compartment through *B* (representing phosphatase). Complete closure of the screw clamp at *B* results in continuous conversion of absorbed glucose to glycogen (a condition known as von Gierke's disease).[5]

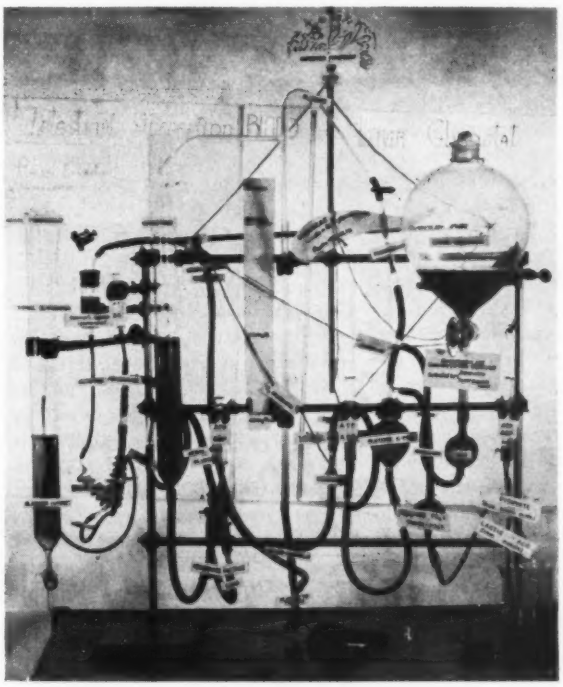

Figure 2

"Glycosuria" results when the fluid level in the blood compartment exceeds that marked 180 mg. per cent. "Renal glycosuria" occurs at normal blood glucose levels if the renal threshold is lowered. Renal filtration of glucose and its reabsorption involve the same type of reasoning.

Gluconeogenesis is illustrated by pumping action on

[1] CANTAROW, A., AND B. SCHEPARTZ, "Biochemistry," 1st ed., W. B. Saunders and Company, Philadelphia, 1954, p. 381.

[2] The valves were constructed from 5-ml. broken-tip Pyrex pipets by cutting the bulb near the middle and with the aid of a stirring motor grinding a tapered soft-glass rod into the constricted end of the pipet bulb. The two halves of the pipet bulb were then resealed with the ground plug enclosed.

[3] Syringe barrels should be liberally greased with Lubriseal.

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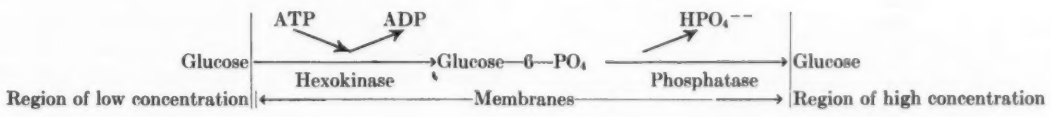


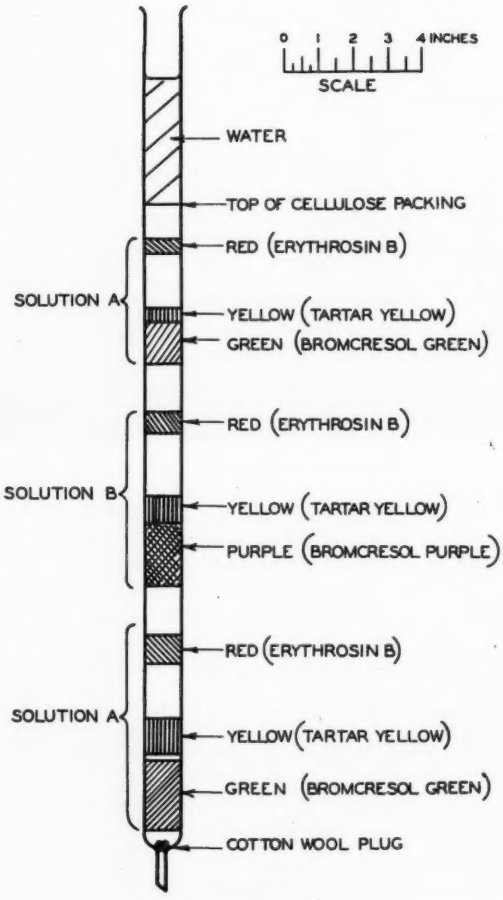
syringe III. The stopcock *C* designates phosphorylase (active and inactive). The effects of epinephrine and glucagon (hyperglycemic factor) are illustrated.[6]

This working model has been employed as an adjunct in teaching for the past two years. The reaction o students has been favorable. After a few demonstrations students are encouraged to carry out the operations and present problems to one another. Since the operation is dependent upon hydrostatic pressures and performance of work through irreversible mechanisms, clearer insight into mass-action effects and energetics is achieved.

[6] SUTHERLAND, E. W., in "Recent Progress in Hormone Research," Academic Press, New York, 1950, Vol. 5, p. 441.

A CHROMATOGRAPHIC DEMONSTRATION

DAVID A. FORSS
Commonwealth Scientific & Industrial Research Organization, Melbourne, Australia



Chromatographic Column

WHEN a "Better Food Exhibition" was held in Melbourne recently, we were asked to demonstrate visually the chromatographic procedure used in the isolation of flavoring compounds. Because of the fire risk and their penetrating odor, organic solvents could not be used and were replaced by water.

A number of indicators and dyes were tested on sheets of filter paper with water at various pH's and those which appeared promising were tested on alumina, silica gel, and cellulose columns. Cellulose columns were the most satisfactory, and two mixtures containing 10 mg. each of three compounds dissolved in 250 ml. saturated aqueous sodium borate were used. Solution *A* contained erythrosine B (tetraiodofluorescein), tartar yellow (tartrazine), and bromcresol green; solution *B* had bromcresol purple in place of bromcresol green.

The column was 60 × 2 cm. and contained 45 cm. of packing. A slurry of Whatman Ashless Powder for Chromatography; Standard Grade was poured into the column in amounts that when compacted with a polyethylene plunger gave 5 cm. of packing. Five ml. of solution *A* was added to the column containing no water above the cellulose, and when the mixture had been adsorbed 5 ml. of water was added, and when this had been taken up by the cellulose, a further 30 ml. water was added. By the time the 30 ml. water had passed onto the cellulose the mixture had separated into an upper red band and a yellow-green band about a quarter of the way down the column. Solution *B* was then added, followed by solution *A*, etc. The diagram shows the column after two lots of solution *A* and one lot of solution *B* had been added.

The eluate was collected in 2- × $^3/_8$-in. test tubes in a fraction collector operating on five-minute intervals.

It is thought that this demonstration might be of use to instructors who wish to illustrate a chromatographic separation with simple apparatus and without organic solvents.

SOME CONSIDERATIONS ON THE ELEMENTRY PHYSICAL CHEMISTRY LABORATORY

B. A. DUNELL and A. E. WERNER
University of British Columbia, Vancouver, Canada

Because many institutions cannot afford enough equipment for the physical chemistry laboratory to allow all students in a laboratory section to do the same experiment on the same day, it is impossible to have complete coordination of laboratory with lecture material. For the same reason, it is impractical to have an introductory laboratory lecture each day. Because of these limitations, and because we were dissatisfed with some of the traditional physical-chemical experiments, we have tried to revise the generally established scheme for the laboratory portion of an elementary physical chemistry course. In addition to our attempt to have all the students do the same or similar things on the same laboratory day, we have tried to emphasize techniques of measurement as distinct from general chemical principles, which are so well documented in a multitude of textbooks and journals.

The laboratory program which we have designed is intended for a small class of students, mainly honor students, who have a good background of general and analytical chemistry and who are taking other courses in chemistry and physics concurrently. The majority of the students taking this course are in their third year.

The aim of emphasizing physical-chemical techniques is furthered by including in the program of exercises and experiments such things as "The Manipulation of Gases," "Methods for Temperature Measurement," "Techniques of Electrical Measurement," "Measurements of Physical Properties of Liquids," and "Calorimetry." In each of these cases the attempt has been made to bring to the students' attention a variety of different methods and pieces of apparatus for measuring the same quantity, wherever possible the methods being ones that are currently used as research tools. Each student is meant to spend a short time working with each piece of apparatus, and making at least one measurement with it. In the laboratory period which is concerned with temperature measurement, for example, there is a preliminary laboratory lecture of from 30 to 40 minutes in which are briefly discussed mercury thermometers, their calibration and the necessity for stem corrections, the Beckmann thermometer and the range of application of the platinum resistance thermometer, the thermocouple, the optical pyrometer, and the hygrometer. In the following two and one-half hours, then, the student must choose from a wide selection a particular mercury thermometer suitable for doing some assigned task, measure a temperature with it, and apply the stem correction as required. He has also to set a Beckmann thermometer to read within a given temperature range; to measure the temperature of a given dry-ice and solvent system with a platinum resistance thermometer which must be wired to its resistance box with the aid of a circuit diagram; to measure a high-temperature system with a thermocouple and potentiometer; to measure the temperature of the interior of a small furnace with an optical pyrometer; to assemble a thermostatic water bath and bring it to a definite temperature; and to measure the moisture content of the laboratory with a psychrometer. In connection with some of these exercises, it should be remarked that in a previous laboratory period on electrical measurements the student has been introduced to the Wheatstone bridge and the potentiometer. Sufficient equipment was to be found in the department to allow 24 students, rotating from one exercise to another, and sometimes working alone and sometimes in pairs, to be accommodated in the one laboratory section. In the period concerned with manipulation of gases, the class of 24 was divided into two parts and in each of two consecutive periods one part was given an introduction to glassblowing. The other half of the class was given an introductory lecture on barometric pressure, storage of gases, reducing valves, vacuum pumps, vacuum systems, simple pressure gages, and the determination of gas density. Then in the laboratory each student was given the opportunity to measure gas density by the simple method of Regnault and with a gas-density balance, to put a vacuum system into operation and use a McLeod gage, and to learn something, even though little, of the technique of dealing with gases. Although it must be agreed that in one three-hour laboratory period a student can get only the briefest introduction to a whole group of techniques, it is the authors' belief that even making the student aware of the existence of methods and apparatus by bringing him into personal contact with them, and having him perform even the simplest operation with them, is of considerable benefit. Manual dexterity with laboratory equipment, achieved by repeated operations of the same kind, is well inculcated in other laboratory courses, in particular by extensive analytical work. Moreover, some of the techniques that the student learns of in the more general experiments are used as tools in later experiments of a less general nature.

Dealing with a laboratory section of only 24 students we have found it possible to have only one student working on each piece of apparatus in many cases. In an experiment on measuring the approximate molecular

weight of organic vapors, for example, eight sets of each of Victor Meyer, Hofmann, and Bleyer and Kohn apparatus were assembled, and after a half-hour laboratory lecture each student was able to do one molecular-weight determination by each of the three methods, spending 50 minutes on each. In an experiment on measuring vapor pressure of liquids one may choose three methods such as the Menzies' Isoteniscope method, the gas saturation method, and a dynamic method to illustrate the technique for measuring vapor pressure. The technique is shown adequately by making the appropriate measurement at one fixed pressure or one fixed temperature; if it is further desired that the variation of pressure with temperature be illustrated, then each student may take his measurement at a different temperature and pool his result with those of the other students doing the same experiment. The pooled data may then be used to illustrate the desired point.

It is of course recognized that the acquisition of isolated experimental techniques does not constitute adequate training in the physical chemistry laboratory. We have therefore collected a carefully considered group of problems which are to be answered experimentally in the laboratory and which require the application of experimental techniques learned earlier, of theoretical material learned from the lecture course or from appropriate reading, and of simple mathematical treatment of the experimental results. These problems are sufficiently long that they require at least two laboratory periods for completion, and one is given to each student at the end of the laboratory course. An example of such a problem is the following: Determine the relation of vapor pressure to temperature for the given sample of unknown liquid, and find its heat and entropy of vaporization per gram. The student must know how to determine vapor pressure, how to set up and control a thermostatic bath, and how to determine the molecular weight of a volatile liquid, as well as be able to analyze his experimental results. Thus, it is intended that solving this "examination problem" will produce some integration of previous laboratory work, will bring attention to the necessity for checking results—since accuracy will be marked—and will emphasize the practical usefulness of the acquired techniques in common chemical problems.

For the most part, the laboratory reports that we require are of the usual type that consist of a statement of the object of the exercise, a short outline of the essential theoretical principles relating to the exercise, a page of tabulated numerical observations recorded during the course of the experiment, a section showing calculation of results from observations, and a final summary of results with a discussion of sources of error. For the first exercise the required report consists of the answers to a number of questions and an outline with specific journal references for an essay on a topic which has required a modest literature research. The reports required for exercises 3, 8, 10, and 11 are very brief, consisting of the answers to some questions and the calculations based on the few quantitative observations that are made. The practical examination involves submission of a detailed report in which the form of presentation and the discussion of results and errors are given weight along with technique and accuracy.

The group of exercises and experiments which constitute our first attempt to put our scheme into action is the following.

Exercise 1: A Library Exercise in which the student is introduced to some of the reference tools of interest to the chemist, and the physical chemist in particular.

Exercise 2: Glassblowing in which the student is introduced to the techniques of handling glass.

Exercise 3: Manipulation of Gases in which the student is introduced to some rules and techniques for handling compressed gases in cylinders and gases in vacuum systems, and two techniques for measurement of gas density.

Exercise 4: Molecular Weight of Volatile Liquids in which a molecular-weight determination is made by each of the Victor Meyer method, Hofmann method, and Bleyer and Kohn method.

Exercise 5: Vapor Pressure of Liquids in which the vapor pressure of a liquid is measured at a particular temperature by the Menzies' isoteniscope and by the gas-saturation method, and the temperature of boiling is observed in a vacuum distillation system at several pressures.

Exercise 6: Physical Characteristics of Liquids in which the density of a liquid is measured at a particular temperature with a Westphal balance and a Davidson gravitometer; the viscosity measured at a particular temperature with an Ostwald viscometer, with a falling sphere viscometer, and a Poiseuille capillary tube; and the surface tension measured at a particular temperature by a capillary rise method, by a Traube Stalagmometer, and by the bubble-pressure method.

Exercise 7: Solubility in Liquids in which the solubility of a gas in water is measured at one temperature using a Bunte gas buret, the solubility of a solid substance in water by the method of Alexejeff using Menzies' apparatus, and the mutual solubility of a partially miscible liquid system studied by a titration method at a fixed temperature.

Exercise 8: Use of Optical Instruments in which the student is introduced to the use of three types of refractometer, to the use of three types of colorimeter, and to the use of a light microscope.

Exercise 9: Vapor-Liquid Equilibria in which the compositions of liquid and vapor in equilibrium with one another in an Othmer still are determined. The compositions of the liquid mixtures (and condensed vapors) are determined by means of a refractometer. Another experiment to determine the molecular weight of a slightly volatile organic liquid by steam distillation is also done.

Exercise 10: Techniques of Electrical Measurements in which the student is introduced to the use of the potentiometer, Wheatstone bridge, mirror and suspension types of galvanometer, a copper coulometer, and two simple types of relay.

Exercise 11: Thermometry in which the student is introduced to the proper use of mercury thermometers, including the Beckmann, to the platinum resistance thermometer, the thermocouple, the optical pyrometer, and wet- and dry- bulb thermometers, and is required to assemble a thermostatic bath and bring it to some constant temperature.

Exercise 12: Calorimetry in which the determinations of heat capacity of gases, heat of reaction, heat of combustion, and heat of vaporization are studied.

At present, these exercises are supplemented by a number of experiments of the usual type to complete the laboratory program for the year.

TECHNIQUES OF DATA SEARCHES IN CHEMICAL LIBRARIES[1]

ROBERT E. MAIZELL
Olin Mathieson Chemical Corporation,
Niagara Falls, New York

THOSE of us literature chemists who work in the chemical industry are confronted every day with requests for supplying data from the literature on the basic properties of pure chemicals. Such data are used by the chemist and engineer as helpful guideposts in the development of chemicals and chemical processes all the way from the test tube stage to the publication of trade literature announcing the commercial availability of the new chemical. It is our purpose to describe some of the sources and techniques used in assembling and evaluating these data. This paper is written from the point of view of the literature chemist rather than that of the physical chemist or the chemical statistician.

Frequently the librarian or chemist will check a variety of literature sources for data in a hit-or-miss way. He may limit his search to such old standbys as the "International Critical Tables." These volumes, while monumental in their day, are now out of date and are hampered by certain basic errors due to inadequate checks of the original proofs. Or the chemist in search of data may feel that the data reported in the popular desk handbooks are 100 per cent authentic and up to date.

It is my thesis that it is possible to proceed systematically down a standard list of secondary and primary sources which will ordinarily reveal the information wanted with maximum speed and with a reasonable degree of accuracy. These sources may be conveniently divided into four groups in order of the ease with which reasonably accurate data are revealed.

Groups 1 and 2 list the sources which are most likely to yield data quickly. Groups 3 and 4 should be consulted if greater precision and validity of data are desired. The titles in each of the four groups suggested here will be followed by a brief description.

GROUP 1

(*a*) "Chemical Materials Catalog" (Reinhold), and other trade literature.

(*b*) "Lange's Handbook of Chemistry" (Handbook Publishers).

(*c*) HODGMAN, "Handbook of Chemistry and Physics" (Chemical Rubber Publishing Company).

(*d*) PERRY, "Chemical Engineer's Handbook" (McGraw-Hill).

(*e*) TIMMERMANS, "Physico-Chemical Constants of Pure Organic Compounds" (Elsevier).

(*f*) Pertinent A. C. S. monographs or other books.

(*g*) Publications of API Project 44.

Manufacturer's trade literature gives very full treatment of physical properties. Original data are frequently presented here. As indicated above, a good starting point is the collection of condensed catalogues from various manufacturers found in the "Chemical Materials Catalog." One point to be noted carefully is whether the properties given are for the technical grade or for the pure chemical.

The handbooks are usually very helpful but do not always refer to the latest sources of information. Also, owing to the broad scope of such publications, handbook editors cannot critically evaluate all sources of data. In any event, the searcher should look for some reference to the recent primary literature or for some other supporting evidence. Timmermans is a unique work which may be described as a data searcher's ideal. Only accurately determined data for pure compounds are given and these are accompanied by full and sometimes critical citations of the original literature.

Books, especially American Chemical Society monographs on specific chemicals, are sources of original data which are sometimes overlooked in this day of emphasis on the journal. It should be noted in passing that while journal articles are fully covered by the various abstracting services, similar analytical indexing is not provided for most books. The new data book just issued by the Dow Chemical Company is a noteworthy compilation of data on several hundred compounds, and it contains some previously unpublished information. The new edition of Landolt-Bornstein should be included in this list, just as soon as the volume on physical properties appears.

GROUP 2

(*a*) BEILSTEIN, "Handbuch der Organische Chemie."

(*b*) HEILBRON, "Dictionary of Organic Compounds" (Oxford).

(*c*) GMELIN, "Handbuch der Anorganische Chemie."

(*d*) MELLOR, "Comprehensive Treatise on...Inorganic Chemistry" (Longmans).

(*e*) KIRK and OTHMER, "Encyclopedia of Chemical Technology" (Interscience).

With the exception of Kirk and Othmer, these sources are representative of the German "Handbuch" in which data from widely scattered journal articles are brought together in a single place. These publications are more

[1] Presented at the 126th Meeting of the American Chemical Society, New York, September, 1954.

difficult and more time consuming to use than those in Group 1, and become quickly out of date. They frequently cite several values for the same constant, or use meaningless general terms such as "slightly soluble." However, they are especially helpful in providing a background for further searching, and they do provide data on lesser known compounds.

GROUP 3

(*a*) SAX, "Handbook of Dangerous Materials" (Reinhold).

(*b*) NATIONAL BUREAU OF STANDARDS, Circular 500: "Selected Values of Chemical Thermodynamic Properties."

(*c*) DREISBACH, "PVT Relationships of Organic Compounds" (Handbook Publishers).

(*d*) SEIDELL, "Solubilities..." (Van Nostrand).

(*e*) BICHOWSKY AND ROSSINI, "Thermochemistry of Chemical Substances" (Reinhold).

(*f*) HUNTRESS, "Organic Chlorine Compounds" (Wiley).

(*g*) JORDAN, "Vapor Pressure of Organic Compounds" (Interscience).

(*h*) AMERICAN PETROLEUM INSTITUTE, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds" (Carnegie Press).

This third group of sources is representative of specialized sources to be used for particular properties or types of chemical. The list will probably vary with the particular interests of the company or institution. These are sources to be used to supplement information gleaned from Groups 1 and 2. It is important to keep the number of sources consulted here down to a reasonable level because of the time factor. As an example of how to use sources in this group, Sax is the basic work to be consulted when quick information on flash point, toxicity, and related information is needed. For specialized information on solubilities, Seidell is the basic reference work. Books covering the field of use or application of a given chemical can be included in this category. There are perhaps hundreds of additional books which could be included in this category, many of which could be found only in large collections such as the New York Public Library or the Chemist's Club Library.

GROUP 4

(*a*) *Chemical Abstracts*, especially 1937–46 collective index, formula index 1920-46, and annual indexes 1947 to date.

(*b*) Other specialized abstracting services.

(*c*) Current issues of journals pertinent to the search.

In theory, a complete search of *Chemical Abstracts* should be made for every chemical being studied, but available time does not always permit this. It may be that most of the basic physical properties sought can be adequately supplied from a search of the first three categories given here, in which case *Chemical Abstracts* need not be consulted at all except to verify doubtful values and to bring the search up to date. In using *Chemical Abstracts* one should note that articles dealing with preparation or use of a compound frequently give physical properties. *Journals* are rich sources of original data. Articles in the *Journal of the American Chemical Society* are especially useful for information on basic properties such as boiling point and refractive index. Trade or commercial magazines frequently have articles with information on properties affecting use, such as toxicity and handling precautions.

OTHER SOURCES

One of the fine points in data searching is knowing when to stop. According to studies by Fussler and the late English documentation specialist Samuel Bradford, while most of the references on any one subject in science and technology can be readily found in a limited list of basic books and journals, the remainder, usually from 25 to 30 per cent, will be widely scattered in a variety of sources in the same and related subject fields. The implication here for data searchers is that it may be wise to place clear limitations on the amount of time spent in ordinary searches before the law of diminishing returns is reached.

If a reasonably careful search still does not reveal badly needed information, one of the following steps may be taken:

(1) The data can be calculated on the basis of other known data by the use of various standard equations and formulas. Hougen and Watson's "Chemical Process Principles" (Wiley) is good source for such formulas. The tabulation of Cox Charts developed by Dreisbach will also prove useful (Handbook Publishers).

(2) It may be possible to infer roughly what the property might be by:

(*a*) Studying data for similar classes of related compounds.

(*b*) Examining related data for the same compound. For example, toxicity tests with animals may give some clues as to the maximum allowable concentration for humans.

(3) Recourse can be made to an expert in the field or to the manufacturer of the product.

(4) It is frequently quicker, easier, and more accurate to determine the data in the laboratory than to spend days in searching the literature. In this event the professional pride of the literature chemist will have to take a back seat.

EVALUATING SUSPECT OR CONFLICTING DATA

Data taken from several sources may vary greatly or data from a single source may seem to be out of line. In determining the reliability of the data found (without making recourse to the physical chemistry laboratory) one should consider several external criteria. The list cited here includes the factors usually cited by *Chemical Reviews* authors, by Egloff (in his A. C. S. monograph) and by Timmermans (*op. cit.*). Egloff also presents a statistical method for comparing data.

The following are some of the criteria to be considered:

(1) The author should be a specialist in the chemical or property being studied and should have a good reputation for careful work.

(2) Specialized works like Huntress' "Organic Chlorine Compounds" or Miner's A. C. S. monograph, "Glycerol" (Reinhold), are to be preferred to the more general handbooks.

(3) The reputation of the publisher or other sponsoring body should be considered. A value sponsored by the National Bureau of Standards, for example, usually is particularly valuable, as are values appearing in the *Journal of the American Chemical Society*.

(4) A paper written to determine a particular physical constant is more reliable than a paper in which the constant is determined incidentally as in the course of a laboratory preparation.

(5) Modern values (later than 1900–1910), and the more modern the better, are usually to be preferred over older figures owing to improvements in techniques and apparatus and advances in knowledge, but this does not mean that older sources of information should be neglected entirely by the labeling of early work as mere alchemy.

(6) The author should give full experimental details. Things to look for include:

(*a*) The extent to which the compound has been purified.

(*b*) The reliability and reputation of the method used, the precision of the apparatus, and the limits of error.

All other things being equal, the lack of such information would greatly reduce or even entirely negate the reliability of the data.

(7) It is frequently a good plan to check in several different sources for values on the same constant. Agreement between two or more modern accurate determinations is considered to be an excellent criterion. In conflicting cases, all values given for the same constant can be cited, or an average of the figures may be given if agreement is reasonably close. Another solution is to take the safest or most conservative values. For example, in a study of ignition temperatures the lowest temperature may be selected so as to provide the greatest safety margin.

(8) In comparing secondary sources, the literature chemist should beware of the possibility that both secondary sources may have copied from the same source which may be erroneous to begin with.

(9) Tables or graphs in which even a single error is detected should be subjected to especially careful scrutiny.

FINAL STEPS

Once all the data have been assembled by systematic consultation of the literature as described above and by suitable laboratory experiments, the information should be promptly recorded on a standard form especially developed for this purpose. Such a standard form could have separate columns for recording the property, values obtained, sources, and date of source. The basic properties which could be included in the form include the following:

Formula
Appearance and form
Molecular weight
Boiling point at various pressures
Crystallizing point
Melting point
Specific gravity at various temperatures
Refractive index
Viscosity
Surface tension
Solubility in water and various solvents
Flash point °F. (give method)
Heat of combustion
Heat of formation
Latent heat of fusion
Latent heat of vaporization
Specific heat
Critical temperature and critical pressure
Dissociation constant
Vapor pressure over a range of temperatures
Pounds per gallon
Toxicity
Storage conditions and containers required

It is strongly recommended that when any one property is being looked up, others be recorded at the same time since considerable future labor can be saved. Several properties of a single chemical are often grouped together in one paper. All completed data sheets should be forwarded to a central point (preferably the library) to avoid duplication of effort. If this is not done, several individuals may look over and over again for the same value.

A complete data file for all chemicals under current investigation and production can help provide a sound basis for research, engineering, technical service, and sales.

ACKNOWLEDGMENT

The author wishes to express his appreciation for helpful comments to Mr. R. W. Forbes, Mrs. M. C. Arthur, and Mr. G. M. Bramann, of the Olin Mathieson Chemical Corporation.

"Our experiences and observations alone never lead to finalities. Theory, however, creates reliable roads over which we may pursue our journeys through the world of observation."

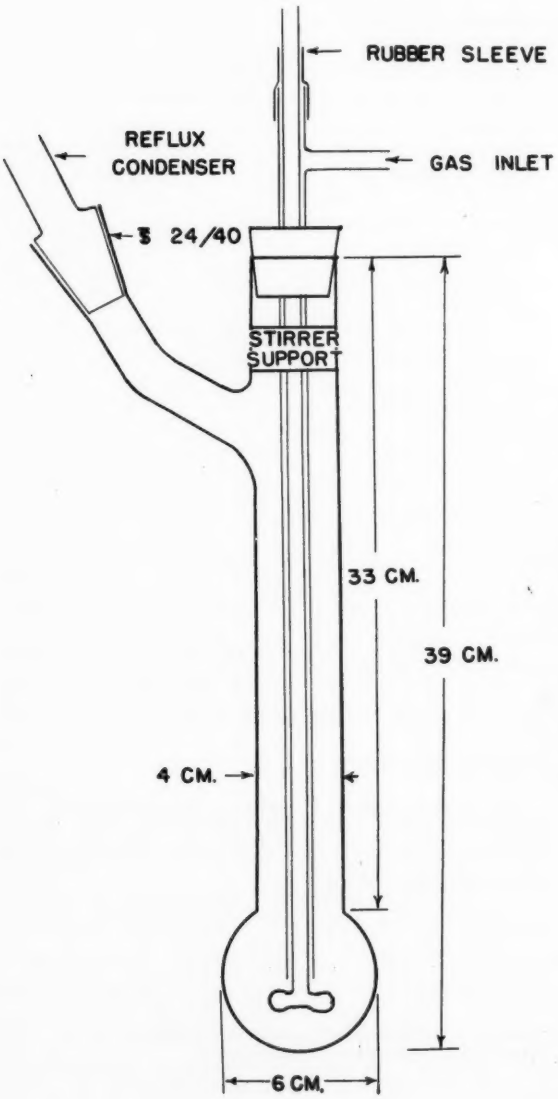
Anton Reiser, 1930

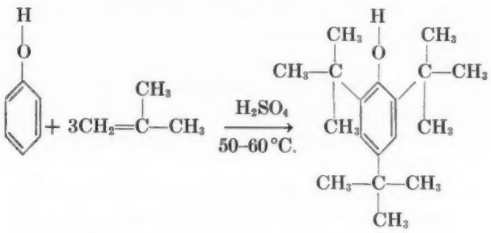
THE PREPARATION OF 2,4,6-TRI-*t*-BUTYLPHENOL

BRUCE G. SOMERS and CLINTON D. COOK
University of Vermont, Burlington, Vermont

RECENT research problems in these laboratories have required large quantities of 2,4,6-tri-*t*-butylphenol, prepared by the alkylation of phenol with isobutylene[1,2] (equation(1)). This preparation has been so satisfactory that we are led to suggest it as an organic laboratory preparation of a modestly advanced nature. The reaction goes smoothly and cleanly to give the product in good yield, it provides an excellent example of a Friedel-Crafts alkylation, and it gives the student experience with one of the techniques of handling a gaseous reactant—usually a mystery to the undergraduate student. A number of second-semester, elementary organic students have carried out the preparation described below, all with good results.

[1] STILLSON, G. H., D. W. SAWYER, AND C. K. HUNT, *J. Am. Chem. Soc.*, **67**, 303 (1945).
[2] COOK, C. D., AND R. C. WOODWORTH, *ibid.*, **75**, 6242 (1953).

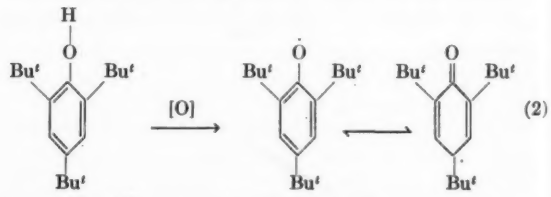




The only appreciable by-products are small amounts of polyisobutylene and, if too little isobutylene is added, mono- and di-*t*-butylphenols. Under the described conditions, these by-products are formed in insignificant quantities.

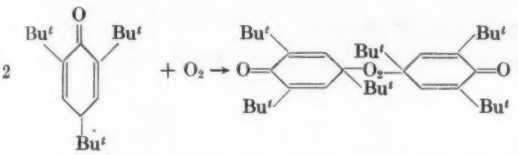
The product, being a "hindered" or "krypto" phenol,[1] provides an example of the effects of steric hindrance. In this phenol the bulky ortho substituents destroy many of the properties generally associated with phenols. Thus, it does not give a color with ferric chloride and is insoluble in both aqueous sodium hydroxide and Claisen's solution. It does, however, react with metallic sodium and with methylmagnesium bromide.

A very striking and simple demonstration of the formation of a free radical is provided by oxidation of this phenol. Shaking a benzene or ether solution with alkaline ferricyanide or lead dioxide rapidly produces the vivid cobalt blue of 2,4,6-tri-*t*-butylphenoxy radical.[2]



Here again is an example of steric hindrance, the bulky tertiary butyl groups preventing the dimerization which

usually accompanies such phenolic oxidations. On standing in air the radical slowly reacts with oxygen to give the light yellow, rather stable bis-(1,3,5-tri-*t*-butyl-2,5-cyclohexadiene-4-one) peroxide.[2] This provides a



(3)

demonstration of a reaction typical of many radicals and, indeed, is the reaction which led Gomberg to the discovery of the first free radical, triphenylmethyl.[3]

While an ordinary three-necked, round-bottomed flask can be adapted to this reaction, an apparatus of the shape shown in the figure is highly desirable, since the increased gas-liquid contact time conserves isobutylene and shortens the reaction time. Such an apparatus is easily constructed by anyone who has an elementary knowledge of glass blowing. The one shown was constructed from the outer jacket of a Victor Meyer apparatus. While not necessary, the bulb on the end is convenient since it allows more play in the stirrer shaft and a bigger blade. The lower stirrer support indicated in the diagram is merely a disc of cork which just fits the bore of the tube. It is a great help in preventing whipping of the stirrer. A fairly high-speed stirrer will lead to more rapid reaction, but an ordinary cone-drive stirrer is adequate.

PROCEDURE

Dissolve 94 g. (1 mole) of phenol in 45 ml. of benzene and add 5 ml. of concentrated sulfuric acid. By means of a water bath heat the solution to 50–60°C. and introduce isobutylene[4] at the maximum rate which can be achieved without loss of large bubbles at the surface of the solution. (The more rapid the rate of stirring, the more rapidly the isobutylene will be adsorbed.) Once the reaction starts, little or no heat will be necessary to maintain the temperature at 50–60°C. When 168 g. (3 moles) of isobutylene have been adsorbed (weigh the apparatus stoppered so that benzene will not be lost) the reaction is stopped. A rough volume calibration is helpful in estimating the quantity of isobutylene which has been adsorbed. At completion the reaction mixture has a volume of approximately 365 ml.

Add sufficient benzene (*ca.* 100 ml.) to dissolve any precipitated 2,4,6-tri-*t*-butylphenol and pour the reaction mixture into a separatory funnel. (The polyisobutylene formed as a by-product does not dissolve in the reaction mixture and will remain as a very viscous and sticky liquid clinging to the sides of the reaction vessel.) Wash the solution with 100 ml. of water, twice with 100-ml. portions of 10 per cent sodium hydroxide, and again with water. Remove most of the benzene by distilling the solution until the pot temperature reaches 120°C. Add 180 ml. of ethanol and warm to dissolve any precipitated material. Filter and allow to crystallize. Filter the crystals at the pump and wash them with a *small* amount of cold ethanol. Reduce by two-thirds the volume of the filtrate and collect a second crop. The yield is about 190 g. (72 per cent). After a second recrystallization the white crystals should melt at 129–130°C. (Reported, 130–131°C.,[1] 131–132°C.[2]) The impure material discolors rather readily, particularly when wet with solvent. It is therefore important thoroughly to dry the material at the pump.

[3] GOMBERG, M., *Ber.*, **33**, 3150 (1900); *J. Am. Chem. Soc.*, **22**, 757 (1900).

[4] Matheson's c. p. grade isobutylene has proved highly satisfactory. A No. 3 cylinder is rather inexpensive, contains enough material (7 lbs.) for a large number of runs, and is of convenient size.

DIVISION OF CHEMICAL EDUCATION, A. C. S.

Nominations

THE following have been nominated for the office of Chairman-elect for the year 1955–56:

Norris W. Rakestraw, Scripps Institution, La Jolla, California
Frank B. Schirmer, Jr., Clemson Agricultural College, Clemson, South Carolina

CONRAD E. RONNEBERG, *Chairman, Nominating Committee*

CONFERENCE ON MICROCHEMISTRY

AN INTERNATIONAL conference on microchemistry will be held in Vienna, Austria, from July 12 to 17, 1955. All branches of pure and applied microchemistry will be included. In addition to the broad program of lectures, there will be exhibits of microchemical apparatus and equipment, and a very ambitious social program is planned. All correspondence relative to the meeting should be addressed to the Generalsekretariat des Vereines Österreichischer Chemiker, Eschenbachgasse 9, Vienna I, Austria.

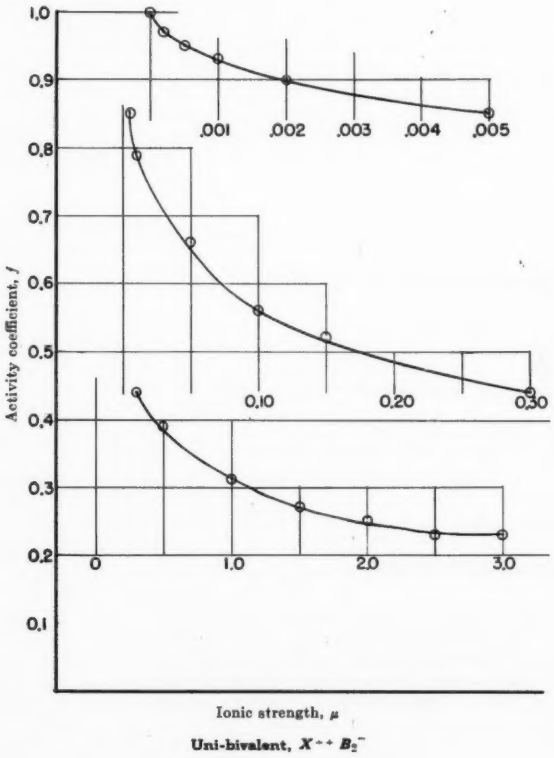
THE USE OF ACTIVITIES IN STUDENT CALCULATIONS

C. SHELDON HART[1]
Carleton College, Northfield, Minnesota

AT PRESENT it is not the general practice to teach activity coefficients to students in beginning quantitative analysis for use in solving problems related to the law of chemical equilibrium. However, two simplified approaches to the subject have been developed for the purpose of presenting the activity concept in a form suitable for students who have not had physical chemistry.

In the first (*1*), the ionization constant or solubility-product constant is assumed to vary with the ionic strength of the solution. When the student has calculated the ionic strength, he uses it to find the p*S* or p*K* which corresponds to it on the graph with which he is furnished. This method has the advantage of simplicity; no new formulas are necessary beyond that for the ionic strength.

[1] Present address: 183 West Lafayette Avenue, Syracuse 5, New York.



In the second (*2*), the ionization constant or solubility-product constant is assumed to be a true, or thermodynamic constant. The relevant expression is derived using activities instead of molar concentrations. Then the student consults a table to locate the activity coefficient which corresponds to the ionic strength he has calculated. This is the procedure which will be discussed.

The advantage of this second method is that it emphasizes the use of activity coefficients. It has the disadvantage that the values given for activity coefficients are those calculated from the Debye-Hückel equation, rather than derived from experiment. Nevertheless, these values are sufficiently accurate for the student to use while learning how to work with activities. When he encounters the more accurate data (*3*) he will be able to use them.

The chief obstacle to using this method is the table. A graph is indispensable; yet when these data are plotted in the usual manner on an 8.5- × 11-inch sheet of paper the result is a curve which is too compressed to give accurate results for the activity coefficient. The necessary extension can be achieved on one page by breaking the curve into three sections, each of which is scaled horizontally (the ionic strength) so as to stretch most of the way across the page. All three curves are referred to the same vertical axis (the activity coefficient) which runs from 1.00 down to zero. Near the top of the graph is the portion covering ionic strengths of 0.00 to 0.005. Just below this is the 0.005 to 0.30 region; and below it is the region from 0.30 to 3.00. This is illustrated in the figure. Students are given three of these graphs: one for univalent, one for uni-bivalent, and one for bi-bivalent electrolytes. Experience has shown that they have no difficulty in finding the activity coefficient once the ionic strength is known.

PRESENTATION TO THE CLASS

(1) What evidence do we have that the mass law fails with electrolytes? When molar concentrations are substituted in the mass law, experiments show that the law, which holds in solutions as dilute as 0.001 molar and below, fails when the ion concentration gets larger, as shown in Tables 1 and 2.

According to the law of chemical equilibrium in the classical form, the solubility-product expression should be the same regardless of the salt concentration. Therefore, the solubility found by calculation will be the same. This is not true experimentally, for in Table

TABLE 1
The "Salt Effect" or "Diverse Ion Effect"
The Solubility of Silver Chloride (4) and Barium Sulfate (5) in Dilute Solutions of Potassium Nitrate at 25°C.

Conc. of KNO_3	*Solubility of AgCl, as found*	$\frac{S^a}{W^b}$	*Solubility of $BaSO_4$, as found*	$\frac{S}{W}$
0.000 *M/L*	1.278×10^{-5} *M/L*	1.00	0.96×10^{-5} *M/L*	1.00
0.001	1.325	1.04	1.16	1.21
0.005	1.385	1.08	1.42	1.48
0.010	1.427	1.12	1.63	1.70
0.036	...	...	2.35	2.45

[a] S = solubility in KNO_3 solution.
[b] W = solubility in water.

1 we see that when the KNO_3 concentration is 0.01 *M* the AgCl is 12 per cent more soluble and the $BaSO_4$ is 70 per cent more soluble than would be expected if the law were true under the circumstances. When the concentration of Na_2SO_4 is 0.01 *M*, $PbSO_4$ is nearly seven times as soluble as the calculation shows it should be (Table 2). Many more data of this kind exist.

(2) *Why* does the law of chemical equilibrium fail like this? To answer this question we must know what is happening in solution. Freezing-point measurements are one of the methods most generally used for finding the effective concentration of ions in solution. In Table 3 we have evidence that the apparent dissociation of a strong electrolyte diminishes when the concentration of the salt is increased. If KCl were actually 100 per cent dissociated in solution we would expect to find the ratio ΔT/molality equal to 2(1.858) = 3.716°C. per mole of dissolved substance. But even at the lowest concentration shown in our table, the ratio is less than 3.716. As the concentration of KCl is increased the ratio grows smaller. This indicates that there are not as many ions in the solution as we would expect to find when we remember that KCl is known to exist as ions even in the crystalline state. It is evident that the salt in solution behaves *as if* it were less dissociated when it is more concentrated.

We believe that interionic attraction causes the decrease in effective concentration of ions. At any instant some ions will be close enough to those ions of opposite charge around them so that they will be as restricted *as if* they were in a molecule. Such "drag" will become more pronounced as the charge in the solution is increased—by more KCl or by any other electrolyte. Thus, we are brought to see the need for taking account of the electrostatic atmosphere around each ion. G. N. Lewis defined ionic strength: "In any solution of strong electrolytes let us multiply the stoichiometric molality of each ion by the square of its valence (or charge). The sum of these quantities, divided by two (since we have included both positive and negative ions), we call the ionic strength, and designate by mu" (*8*).

We then proceed to calculate the ionic strength for all common types of electrolyte, noting that when there are several electrolytes in solution the ionic strength is the sum of the individual values.

The mass-action law of chemical equilibrium is a limiting law—one which applies more closely as the concentrations approach zero. (This reminds us of another limiting law: the ideal gas law, which fails at high concentrations because the gas molecules have an attraction for one another, and occupy some space.) The mass-action law fails at high concentrations of ions because oppositely-charged ions tend to cling together, so that at any instant many ions are not free. But as we approach zero concentration the ions are so far apart that they are not likely to cling together momentarily; and so practically all exist as free ions. That we are justified in using molar concentrations under these circumstances is shown by the data in Tables 1 and 2; the law holds better in more dilute solutions. As we consider the case for the more concentrated solution where the ions are close enough together so that at any moment many of them will be inhibiting one another's free movement, it is easy to see that the actual concentration of free ions will be less than their molar concentration. And yet when we substitute molar concentrations we are assuming that all of the ions are free. It is no wonder that the ideal form of the mass law does not hold, except at high dilutions.

TABLE 2
The Common Ion Effect
Solubility of Lead Sulfate in Solutions of Sodium Sulfate at 25°C. (6)

Conc. of Na_2SO_4	*Solubility of $PbSO_4$, as found (B)*	*Solubility of $PbSO_4$, calc. from Ksp (C)*	$\frac{B}{C}$
0.000 *M/L*	15.2×10^{-5} *M/L*	15.2×10^{-5} *M/L*	1.00
0.001	2.4	2.31	1.04
0.01	1.6	0.23	6.96
0.02	1.4	0.12	12 3
0.04	1.3	0.058	22 5
0.10	1.6	0.023	69 6
0.20	2.3	0.012	200
0 50	2.3	0.0046	500

(3) How do we solve this problem of making the mass law apply to solutions of electrolytes? In trying to get a law which will represent reality for the solutions we use, we have the possibility of developing a new expression which will involve as many as possible of the relevant factors. When such an expression has

TABLE 3
Depression of the Freezing Point of Water by Potassium Chloride (7)

Molality of KCl solution	*ΔT, the measured freezing-point depression*	*Ratio* = $\frac{\Delta T}{\text{molality}}$
0.00506	0.0184	3.64
0.00963	0.0348	3.61
0.01648	0.0590	3.580
0.03170	0.1122	3.539
0.05818	0.2031	3.491
0.11679	0.4014	3.437

been worked out we discover that it is not practical to use. We come to the conclusion that it is better to retain the simple form of the mass law and apply correction factors which can vary with the concentration. (This is the same type of "solution" in use with the ideal gas law for the purpose of adapting it to conditions far from ideal.) For the mass law these correction factors are called "activity coefficients." The mathematical product of its molar concentration and its activity coefficient is called the activity of that species. Activity may be considered as the active concentration —the apparent concentration as judged by its effects which we can measure. There are several methods for determining the activity, among them the measurement of colligative properties; but all of these are too involved to be presented at this point. Once the activity is known for a given set of conditions and ionic strength, the activity coefficient can be calculated for use elsewhere as needed.

It is evident that activity, being based upon direct measurements, is likely to be the most nearly correct value to substitute for the concentration. As we look at the graph which shows how activity coefficients vary with ionic strength, it is understandable that the mass law *should* fail when molar concentrations of ions are used, because the active concentrations will diminish as the ionic strength builds up; while the molar concentration is not influenced by the changes in ionic strength as long as none of that species is added. The activity coefficients which we use were calculated from the Debye-Hückel equation, and are only approximately correct; but they are entirely satisfactory for use in introducing the subject, and they give nearly correct results while permitting considerable simplification.

(4) How does one work problems involving activities? There are four steps: (*a*) Derive the formula using activities instead of molar concentrations, merely by multiplying each molar concentration by its activity coefficient *f*; (*b*) calculate the ionic strength; (*c*) using the appropriate graph, find the activity coefficient which corresponds to the ionic strength; (*d*) substitute data and solve.

Two or three of the problems given below are worked in detail for the class, to indicate how this is done. The simplified procedure outlined gives results which are sufficiently good to warrant use of it when introducing the activity concept to students in quantitative analysis. During the derivations the following additional information comes to light:

(*a*) The activity coefficient for solids, un-ionized molecules, and nonelectrolytes is 1.00, for practical purposes.

(*b*) Activity coefficients for positive and negative ions of the same valence are, for practical purposes, the same. This is reasonable as a first approximation, since they are together in the same environment, and the "drag" ought to be somewhere near the same.

Students are expected to derive the other formulas for themselves. To aid them they are given the following.

NOTATION AND FORMULAS

( ) = the concentration expressed in moles per liter
μ = ionic strength
f_{H+} = the activity coefficient (of the hydrogen ion)
a_{H+} = the activity (of the hydrogen ion)
= (H^+) (f_{H+})

(1) Solubility of a uni-univalent electrolyte like AgCl:

$$Ksp = (Ag^+)\ (Cl^-)f^2;\ (Ag^+) = \frac{\sqrt{Ksp}}{f}$$

(2) Solubility of a uni-univalent electrolyte like Ag_2CrO_4:

$$Ksp = (Ag^+)^2\ (CrO_4^{--})f^3;\ (CrO_4^{--}) = \frac{1}{f}\sqrt[3]{Ksp/4}$$

(3) Weak acid like acetic:

$$(H^+) = \frac{\sqrt{K(HAc)}}{f}$$

$$a_{H+} = f(H^+) = \sqrt{K(HAc)}$$

(4) Buffer composed of acetic acid and sodium acetate:

$$(H^+) = \frac{K(HAc)}{(Ac^-)f^2}$$

$$a_{H+} = \frac{K(HAc)}{(Ac^-)f}$$

(5) Hydrolysis of a salt like sodium acetate:

$$K_h = \frac{Kw}{K_a} = \frac{(OH^-)(HAc)f}{(Ac^-)f}, \text{ etc.}$$

Since the ratio of the activity coefficients for two univalent ions is unity, by the Debye-Hückel relationship, it is evident that the hydrolysis formula will be the same as if no activity coefficients were used.

(6) For a strong acid or strong base the activity is equal to the normality multiplied by the activity coefficient. Note that a pH meter is calibrated in terms of the pa_{H^+}—the effective and *not* the molar concentration of hydrogen ions.

ILLUSTRATIVE EXAMPLES

Example 1

Calculate the solubility of barium sulfate in a solution which is 0.1 *M* in NaCl and 0.05 *M* in $Mg(NO_3)_2$. $Ksp = 1 \times 10^{-10}$, (*a*) without using activities, (*b*) using activities.

Solution.

(*a*) Solubility = $(Ba^{++}) = (SO_4^{--}) = \sqrt{Ksp} = 1 \times 10^{-10} = 1 \times 10^{-5}\ M/L$

(*b*) *Step 1:* $Ksp = (Ba^{++})(SO_4^{--})f^2$, and so solubility $= (Ba^{++}) = (SO_4^{--}) = \dfrac{\sqrt{Ksp}}{f}$

Step 2: Ionic strength of 0.1 M NaCl = 0.1
Ionic strength of 0.05 M $Mg(NO_3)_2$ = 0.15
Ionic strength of $BaSO_4 = 10^{-5}$ = negligible
Total ionic strength = 0.25

Step 3: Since we want f for $BaSO_4$ we consult the bi-bivalent chart and find, for $\mu = 0.25$, that $f = 0.228$

Step 4: Solubility $= \dfrac{\sqrt{1 \times 10^{-10}}}{0.228} = 4.39 \times 10^{-5}\ M/L$

Comments.

(1) Using activities gives a result which is 4.39 times as large as that by the classical method of calculation. This larger result is reasonable because we know that ions are taken out of effective circulation by interionic attraction. More barium sulfate dissolves in order to maintain a sufficient quantity of really "free" ions to satisfy the ion-product relationship.

(2) Note that we are not interested in the activity of the ions, but rather in the molar concentration —which is the *total* quantity of barium sulfate in solution. The fact that this increases means that the solubility of barium sulfate has increased. We want to avoid this because we are interested in getting as complete precipitation as we can.

Example 2

Calculate the solubility of barium sulfate in a solution which is 0.10 M in ammonium sulfate, (*a*) without using activities, (*b*) using activities.

Solution.

(*a*) Solubility $= (Ba^{++}) = \dfrac{Ksp}{(SO_4^{--})} = \dfrac{1 \times 10^{-10}}{(0.10)} = 1 \times 10^{-9}\ M/L$

(*b*) *Step 1:* Since $K = (Ba^{++})(SO_4^{--})f^2$, solubility will $= (Ba^{++}) = \dfrac{Ksp}{(SO_4^{--})f^2}$

Step 2: Ionic strength of ammonium sulfate = 0.3
Ionic strength of barium sulfate = negligible
Total ionic strength = 0.3

Step 3: The activity coefficient for a bi-bivalent species corresponding to an ionic strength of 0.3 is 0.22

Step 4: Solubility $= (Ba^{++}) = \dfrac{1 \times 10^{-10}}{(0.1)(0.22)^2} = 2.07 \times 10^{-8}\ M/L$

Comments.

(1) Using activities, the solubility is $\dfrac{2.07 \times 10^{-8}}{1 \times 10^{-9}} =$ 20.7 times as large.

(2) The purpose of adding a slight excess is to diminish the solubility of a precipitate. The answer to (*b*) shows that if we add too much of the common ion we can *increase* the solubility instead of decreasing it as we intended to do.

Example 3

For a solution of acetic acid which is 0.12 M, calculate (*a*) the (H^+) without using activities, (*b*) the (H^+) using activities, (*c*) the a_{H+}.

Solution.

(*a*) $(H^+) = \sqrt{K(HAc)} = \sqrt{1.8 \times 10^{-5}\ (0.12)} = 1.47 \times 10^{-3}\ M/L$

(*b*) *Step 1:* $(H^+) = \dfrac{\sqrt{K(HAc)}}{f}$

Step 2: Ionic strength $= 1.47 \times 10^{-3}$

Step 3: Activity coefficient = 0.955

Step 4: $(H^+) = \dfrac{\sqrt{1.8 \times 10^{-5}\ (0.12)}}{(0.955)} = 1.54 \times 10^{-3}\ M/L$

(*c*) $a_{H+} = (H^+)f = \sqrt{K(HAc)} = \sqrt{1.8 \times 10^{-5}\ (0.12)} = 1.47 \times 10^{-3}\ M/L$

Comments.

(1) It is interesting to note that even the low concentration of ions from dilute acetic acid will have some effect on its dissociation. When we take account of the ionic strength we find that the (H^+) is 1.54/1.47 = 1.05, or 5 per cent larger than if we had neglected the effect due to its own ions.

(2) It is also of interest to note that our approximate methods for calculation of (H^+) and a_{H+} in parts (*a*) and (*c*) must give the same numerical result.

Example 4

For a solution which is 0.10 M in acetic acid and 0.17 M in sodium acetate, calculate (*a*) the (H^+) and the pH, (*b*) the a_{H+} and the pa_{H+}.

Solution.

(*a*) $(H^+) = \dfrac{K(HAc)}{(Ac^-)} = \dfrac{1.8 \times 10^{-5}\ (0.1)}{(0.17)} = 1.06 \times 10^{-5}\ M/L$

pH = 4.98

(*b*) *Step 1:* Since $K = \dfrac{(H^+)(Ac^-)f^2}{(HAc)}$, $(H^+)f = a_{H+} = \dfrac{K(HAc)}{(Ac^-)f}$

Step 2: Ionic strength of sodium acetate = 0.17
Ionic strength of acetic acid $= 10^{-5}$ = negligible
Total ionic strength = 0.17

Step 3: Activity coefficient for a uni-univalent electrolyte when ionic strength is 0.17 = 0.71

Step 4:

$$a_{H+} = \frac{1.8 \times 10^{-5}\ (0.10)}{(0.17)\ (0.71)} = 1.49 \times 10^{-5}\ M/L$$

$pa_{H^+} = 4.83$

TABLE 4
Solubility of Lead Sulfate in Sodium Sulfate Solutions at 25°C.

Conc., Na_2SO_4 M/L	Ionic str.	Activity coeff.	Solubility of $PbSO_4 \times 10^5$ M/L: Calc. from activ. A	Found by exp. B	Calc. by class. meth. C	Ratios: $\frac{B}{A}$	$\frac{B}{C}$
0.001	0.003	0.77	3.90	2.4	2.31	0.62	1.04
0.01	0.03	0.52	0.85	1.6	0.23	1.88	6.96
0.02	0.06	0.42	0.66	1.4	0.12	2.12	12.3
0.04	0.12	0.303	0.62	1.3	0.058	2.10	22.5
0.10	0.30	0.22	0.48	1.6	0.023	3.33	69.6
0.20	0.60	0.164	0.44	2.3	0.012	5.23	200
0.50	1.50	0.103	0.44	2.3	0.0046	5.23	500

Comments.

(1) The calculations show that the active concentration of hydrogen ion in the buffer solution is 1.49/1.06 = 1.41, or 41 per cent greater than the classical calculation would indicate. The importance of using activity coefficients when calculating the pH of buffers is evident.

(5) What evidence do we have of the practical value of this procedure for calculation? The results in column A in Table 4 were calculated from the data in Table 2 by using the formula $(Pb^{++}) = Ksp/(SO_4^{--})f^2$, where $Ksp = 2.31 \times 10^{-8}$. The ratios in the last two columns of Table 4 show that the use of activity coefficients by the method proposed here produces results much closer to experimental values than the classical method of calculation. Heisig's values are given in Table 5.

TABLE 5
Ionic Strengths and Activity Coefficients[a]

Ionic strength	Activity coefficients: Uni-univalent A^+B^-	Uni-bivalent $X^{++}B_2^-$	Bi-bivalent $X^{++}Y^{--}$
0.0001	0.99	0.98	0.95
0.0002	0.98	0.97	0.94
0.0005	0.97	0.95	0.90
0.001	0.96	0.93	0.86
0.002	0.95	0.90	0.81
0.005	0.92	0.85	0.72
0.01	0.89	0.79	0.63
0.05	0.81	0.66	0.47
0.1	0.76	0.56	0.33
0.15	0.72	0.52	0.28
0.3	0.66	0.44	0.22
0.5	0.62	0 39	0.18
1.0	0.56	0.31	0.13
1.5	0 52	0.27	0.10
2.0	0.50	0.25	0.09
2.5	0.49	0.23	0.08
3.0	0.48	0.23	0.075

[a] From HEISIG, G. B., "The Theory and Practice of Semimicro Qualitative Analysis," W. B. Saunders Company, Philadelphia, **1943**, p. 94.

ACKNOWLEDGMENT

We are indebted to Miss Marian C. Chalmers for devising the arrangement of the graph of the activity coefficient which is described here.

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GLASCOL ADAPTER

JEAN V. JOHNSTON
Connecticut College, New London, Connecticut

THE usefulness of the 500-ml. size of a hemispherical Glascol heating mantle can be increased by fitting it with a round-bottomed, deep-form sand bath which is four inches in diameter, and which contains a suitable amount of Wood's metal. Flasks of less than 500-ml. capacity as well as the 500-ml. flasks for which the mantle was designed can all be heated equally conveniently by the same size of mantle.

TEXTBOOK ERRORS[1]

II: Brownian Motion and the Stability of Colloids

KAROL J. MYSELS
University of Southern California,
Los Angeles, California

THE fact that colloidal solutions are frequently quite stable and their particles do not sediment when kept in bottles under ordinary laboratory conditions, is frequently[2] attributed to the incessant agitation of Brownian motion.

This explanation has a small grain of truth in it. Thermal agitation always tends to counteract the forces of gravity acting on a particle and when these forces are small, it may indeed give a practically uniform distribution. As the particle size increases, however, and the gravitational forces grow proportionately, thermal agitation leads only to an equilibrium distribution in which the concentration decreases with height. Since this equilibrium is the result of a balance between the gravitational forces (which for a particle in water are proportional to its volume V, the gravitational constant g, and the difference of densities $d - 1$) and the kinetic energy of the particle (which is proportional to RT/N), the ratio of concentrations C_1 and C_2 at two levels differing by h, is given[3] by the modified barometric equation:

$$\ln(C_1/C_2) = Vh(d - 1)gN/RT$$

With the aid of this formula we can calculate the largest size of particle which would show less than a twofold difference of concentration at equilibrium between the top and bottom of a bottle 15 cm. in height. The corresponding radii r_1 and molecular weights M_1, for spherical particles of gold, sulfur, and protein, are shown in the table. Obviously these are toward the lower edge of the colloidal range. Hence, thermal agitation cannot account for the experimentally observed uniformity of these and much coarser suspensions.

	For $C_1/C_2 = 2$ at 15 cm.			For v_2 = 1 cm./hour	
	r_1, mμ	M_1	v_1, cm./year	r_2, μ	M_2
Gold	3.0	1.2×10^6	1.2	0.26	7.8×10^{11}
Sulfur	7.8	2.8×10^6	0.43	1.1	6.1×10^{12}
Protein	12.0	5.6×10^6	0.33	1.9	2.2×10^{13}

The correct explanation lies in the fact that the *rate* of sedimentation, v_1, of these particles is incredibly slow, of the order of a year per centimeter, as shown in the table. By Stokes' law this rate increases with the square of the radius but does not become of the order of a centimeter per hour until particles reach the large sizes shown in the last columns of the table. Hence, not only is the rate of attainment of equilibrium very slow, but the slightest convection currents caused by least temperature differences are sufficient to stir the suspension to practical uniformity.

Thermal convection currents are difficult to eliminate completely, especially in large vessels. Elaborate thermostatting[4, 5] or enclosure by good insulators[5, 6] has been used to produce quiescent solutions in which equilibrium can be approached. Under these conditions sedimentation occurs unmistakably and the logarithmic distribution holds over a wide range,[5] showing conclusively that it is convection, and not Brownian motion which is responsible for the uniformity observed under usual laboratory conditions.

[1] Suggestions of material suitable for this column are eagerly sought and will be acknowledged. They should be sent with as many details as possible to K. J. M. at the above address.

[2] Since the purpose of this column is to prevent the spread and continuation of errors and not the evaluation of individual texts, the source of the errors discussed will not be cited. The error must occur in at least two independent standard books to be presented.

[3] *E. g.*, SVEDBERG, T., "Colloid Chemistry," The Chemical Catalog Co., New York, **1924**, p. 97.

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"It ought to be esteemed much less disgraceful to quit an error for a truth than to be guilty of the vanity and perverseness of believing a thing still, because we once believed it."

Robert Boyle, 1627–91

MAGNETIC SUSCEPTIBILITY BALANCE

JUDSON L. IHRIG and ROBERT G. CALDWELL
University of Hawaii, Honolulu, Hawaii

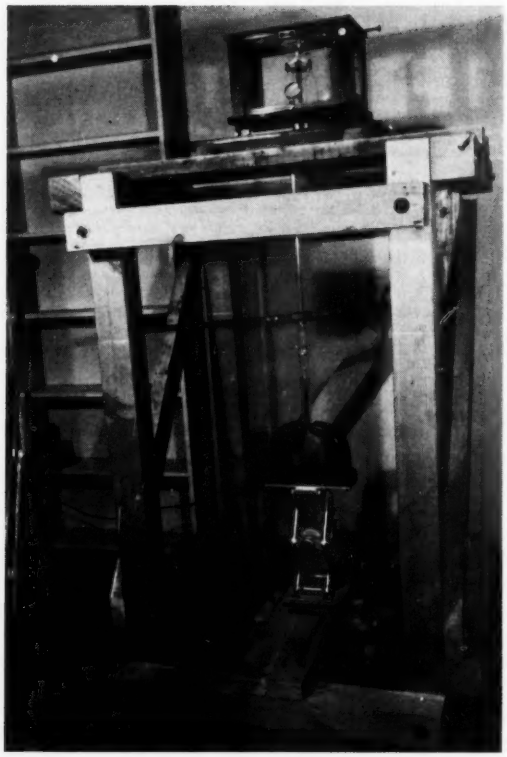


Figure 1

In recent years magnetic susceptibility measurements have been applied to diverse fields of chemistry. Magnetic susceptibility now appears to be taking its place with dipole moment, molecular spectroscopy, and X-ray diffraction as a common tool in the study of molecular structure. Because of this trend, consideration has been given to the inclusion of magnetic susceptibility experiments in the laboratory courses in physical chemistry or instrumentation. Schuler[1] has described a very simple instrument for instructional purposes. This apparatus, though practical for laboratory exercises, does not possess the sensitivity or precision needed for research work.

Despite the advantages of combining in one instrument both teaching and investigational functions, some laboratories have been reluctant to set up equipment for magnetochemical work because of the expense involved. The costly item of equipment is the large electromagnet usually employed and its power supply. The use of a permanent magnet instead may frequently make the construction of an instrument practical for such laboratories whose budgets are limited.

This paper describes the construction and operation of a magnetic susceptibility balance which may be built easily and economically. Its simplicity commends it as an instrument for laboratory instruction; at the same time it has proved sensitive enough for magnetochemical research.

THE GOUY METHOD

The most usual method for the determination of magnetic susceptibility is that of Gouy. The principles of the method have been given in detail by Selwood.[2,3] Briefly, the procedure consists of measurement of the force exerted upon a cylindrical tube containing the sample in the presence of a magnetic field. This force is related to the magnetic susceptibility of the material by the expression:

$$F = {}^1/_2(K_1 - K_2)\,(H_1^2 - H_2^2)A$$

where K_1 and K_2 are the volume susceptibilities of the substance and the surrounding medium, respectively. H_1 and H_2 are the magnetic field strengths at the bottom and top of the cylindrical tube, respectively, and A is the cross-sectional area of the tube. In practice, the tube is placed in the field so that its lower end is in the region of greatest intensity and its upper portion is in a region of negligible field; this has the effect of eliminating H_2 from the calculations. K_2 is the volume susceptibility of air; it too may be disregarded if the air surrounding the sample is replaced with a gas, such as hydrogen or nitrogen, which has a very small volume susceptibility.

In the Gouy method this force along the axis of the tube may be equated to $g\Delta w$, where g is the gravitational constant and Δw is the apparent change in weight of the sample due to the influence of the magnetic field.

Substances whose electrons are all paired are repelled by the field; they have negative susceptibilities and are said to be diamagnetic. Other substances (free radicals and certain salts of transition metals, for example) which possess one or more unpaired electrons are attracted to the field and are called paramagnetic. Their susceptibilities are positive in sign, as are their Δw values.

[1] Schuler, R. H., J. Chem. Educ., **27**, 591–4 (1950).

[2] Selwood, P. W., "Magnetochemistry," Interscience Publishers, Inc., New York, **1943**.

[3] Selwood, P. W., in A. Weissberger, Editor, "Physical Methods of Organic Chemistry," 2nd. ed., Interscience Publishers, Inc., New York, **1954**, Part 3, pp. 2451–90.

The experimental procedure consists of weighing the sample in and out of the applied magnetic field. Because the area A and the field H_1 are difficult to measure accurately, the apparatus is usually calibrated with two substances of known susceptibility. Air, water, benzene, and nickel chloride solutions are among the common calibrating agents. It is best to choose calibration substances which give rise to forces of approximately the same magnitude expected for the unknown substances under investigation.

THE APPARATUS

Figure 1 shows the complete apparatus. The sample tube is suspended by a fine copper wire from the arm of an old Kuhlmann microbalance. An outer glass jacket encloses the sample tube to protect it from drafts which would otherwise cause deflections of the tube several times as great as those produced by the magnetic field. The details of the suspension are shown in Figure 2. The sample tube itself is made of 13-mm. Pyrex tubing and is about 20 cm. in over-all length. The tube is made sufficiently long so that the upper end will be in a region of negligible field strength when the lower end is positioned between the pole pieces of the magnet as shown in the drawing. The cross-sectional area is made as large as possible so as to have the maximum amount of sample acted upon by the field. Care must be taken, however, to prevent actual contact of tube with jacket, and between jacket and pole pieces. Closure of the tube is a $^{7}/_{25}$ ground-glass joint.

The glass housing is made in two sections, the lower end of 32-mm. Pyrex tubing narrowing to 18 mm. so as to fit between the magnet pole pieces. This lower section of about 14 inches is connected to the fixed upper portion, of 18-mm. tubing and 25 inches long, by means of a $^{29}/_{42}$ joint. This allows access to the sample tube. The upper portion is fixed to the balance support with a rubber gasket in such a manner as to prevent drafts. It is also supported by a sponge-rubber ring clamped in a brace of brass strip attached to the main apparatus frames. This may be seen in Figures 1 and 3.

The latter figure is a close-up of the magnet and its mounting. The magnet support is a heavy-duty automobile scissors jack firmly bolted to the base of the apparatus frame. This jack was chosen because of its high lift and also because the lifting mechanism has both a coarse and a fine adjustment which permits an accurate and reproducible positioning of the magnet poles about the sample tube. Moreover, its cost (about $12) is less than half that of a similar laboratory jack. When raised into position around the tube, the magnet is still some three feet from the microbalance and has no detectable effect upon the weighings. During measurement of the weight of the sample and tube, the magnet is lowered to its extreme position which results in a negligible field about the sample.

The magnet itself is an Alnico magnetron magnet originally used in one of the larger portable radar trailers. These may still be found in the surplus market or in salvage yards where they are used to pick up nails and bolts. Another source is old conveyer machinery where many were installed to remove steel filings and chips from the material being processed. The magnet shown was purchased in poor condition for $5. It is important to obtain the largest size possible in order that the poles have a reasonable diameter. The larger the diameter of the poles, the larger the volume of homogeneous field H_1, and the greater the reproducibility of the measurements. The magnet used in the present apparatus is fitted with truncated conical pole pieces of soft iron with faces 1.9 cm. in diameter. The pole gap is 2 cm. This arrangement gives a sufficient volume of homogeneous field to permit the vertical positioning of the tube to be done simply by eye. Most surplus mag-

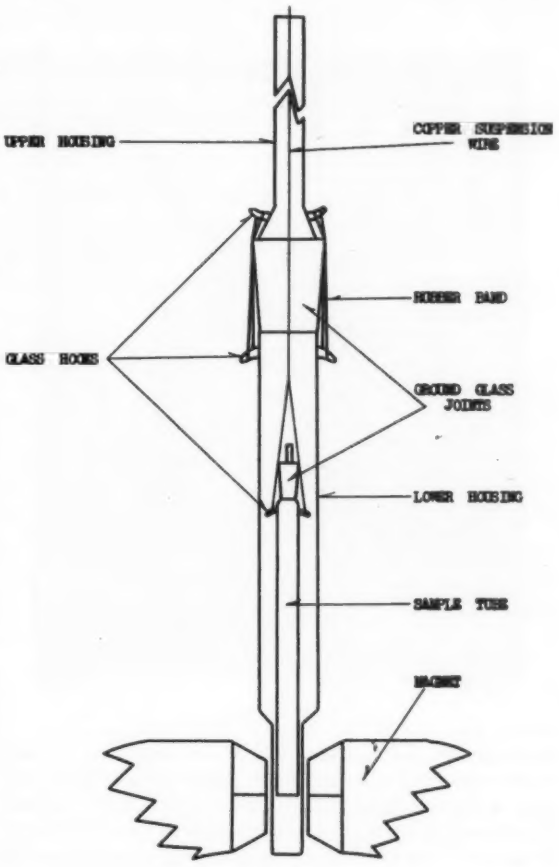


Figure 2

nets need recharging, which is readily done. In this case the magnet was wrapped with 318 turns of No. 10 insulated copper wire and a momentary current of 400 amperes at 75 volts was passed through. This was supplied by a standard d.-c. welding outfit. A field strength of about 5550 gauss was obtained.

The whole apparatus is supported by a sturdy frame made of 4-×4-inch timbers fastened with 9-inch machine bolts. Cross bracing and platforms for the mag-

net assembly and the microbalance are of 2-×4-inch lumber. The balance is supported by a thick glass plate insulated from the frame by four large rubber stoppers. This construction is essentially free of troublesome vibrations.

The balance itself is a costly item, although with the now prevalent practice of having organic analyses performed by outside professionals, many laboratories have sensitive balances which are no longer in constant use. The Kuhlmann model used with this apparatus was particularly easy to modify. It was necessary only to remove the pan-arrest mechanism. On balances with pan arrests operating from the inside of the case, it is also necessary to drill a small hole directly under the left-hand pan stirrup to permit attachment of the suspension wire. With the fairly low field strengths ob-

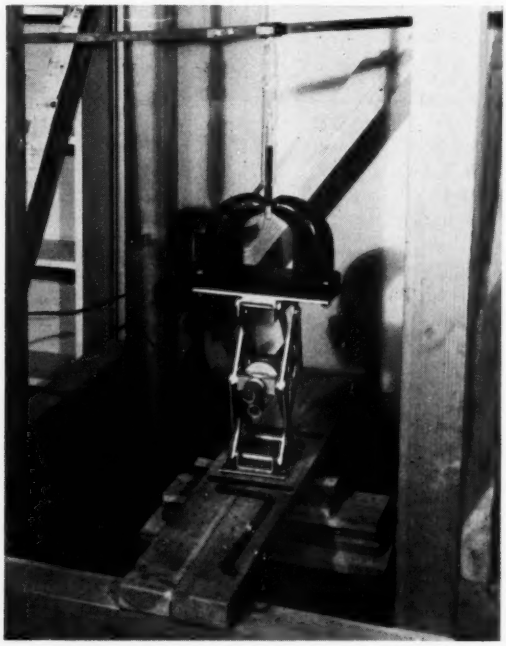


Figure 3

tainable with inexpensive magnetron magnets it is necessary to use a rather sensitive balance. The large, old type of instrument with a sensitivity of $^1/_{50}$ or $^1/_{100}$ mg. is, however, a satisfactory alternative to a microbalance. In general, the greater the field strength available, the more leeway one has in the choice of balance.

OPERATION AND PERFORMANCE

The experimental procedure consists of the weighing of sample and tube both in and out of the magnetic field. The difference in weight Δw may then be related to the volume susceptibility of the material as mentioned previously. First, the filled sample tube is attached to the suspension wire and the lower jacket fitted. After it is certain that there is no contact between tube and jacket, the apparatus is allowed to come to thermal and mechanical equilibrium for 30 minutes. Then the actual weighings are made. It was found that reproducible results were obtained with a series of six weighings made alternately with, and then without the presence of the field. Since microweighings are always subject to thermal deflections caused by the presence of the operator, it is necessary to devise a routine procedure in which the number of operations and their time of duration are held fixed. Only in this way will runs on different substances be comparable with each other and with the calibration values. The exact details of a standardized procedure, which depend upon the balance used and the environment of the entire apparatus, will almost automatically suggest themselves to the operator. In any case, the routine is easy to devise and use, requiring no more practice than is necessary for any precision instrument.

With the equipment described, a precision in weighing of from ±2 to 3 micrograms was obtained. Calibration with water and air showed that this precision corresponded to a volume susceptibility increment of from 1.2 to 1.8 $\times 10^{-10}$ c.g.s. units. Since all but a few literature values of susceptibility are given to only $\pm 1 \times 10^{-9}$ c.g.s. units, the apparatus was considered sufficiently sensitive. Cross checks of the calibration were made using acetone and benzene. The value for acetone was in agreement with the literature value to better than one part in 500, and that for benzene was higher than the literature value by two parts in 600.

These calibrations demonstrate the qualities of this simple apparatus. The equipment was used successfully in an investigation of semiquinone-type intermediates in the oxidation of benzoin to benzil.[4]

ADVANTAGES AND LIMITATIONS

The principal advantages of this apparatus are its simple construction and its low cost which did not exceed $25, since a balance was available. The ease of operation, compared with more complex apparatus, makes the outfit suitable for use in physical chemistry and instrumentation laboratory courses.

The major limitation is that imposed by the use of permanent magnets in general, *i. e.*, a nonvariable field strength. Although the extreme steadiness of permanent magnet fields is of advantage in work where each run is of many hours duration, the absence of field control makes it impossible to make a magnetic check for the presence of ferromagnetic impurities. Thus, the instrument is unsuited for catalytic and solid-state investigations as well as for absolute measurements on many "pure" inorganic salts which frequently have minute traces of ferromagnetic substances. It is true that fields of permanent magnets may sometimes be varied, but not in a simple, inexpensive fashion. The present design, then, is limited to studies of diamagnetic organic substances, free radicals, and certain selected inorganic compounds. Even if the presence of ferromagnetics is

[4] IHRIG, J. L., AND R. G. CALDWELL, to be published.

suspected, however, the apparatus may be used to measure susceptibility *changes* as might arise in the course of a reaction.

A less severe limitation is that the apparatus as described is useful for measurements at one temperature only. To make measurements at temperatures different than ambient, it is necessary only to make the jacket surrounding the sample tube in the form of a Liebig condenser and circulate through it a liquid of the desired temperature. However, extremes of temperature, high or low, demand more elaborate accessories. These are described by Selwood.

In conclusion, it is hoped that the rather detailed exposition of a simple magnetic susceptibility balance will help to promote further investigation in a fascinating field. Those institutions who have not entered this work because of the expense may find this version of the apparatus suited to their needs.

NATIONAL COOPERATIVE UNDERGRADUATE CHEMICAL RESEARCH PROGRAM

ETHALINE CORTELYOU
Armour Research Foundation, Chicago, Illinois
W. P. CORTELYOU
Roosevelt University, Chicago, Illinois

For the 1955–56 school year the National Cooperative Undergraduate Chemical Research Program (NaCUR) offers 19 projects for student participation. The outline used for each project is:

(*a*) Typical unit assignment
(*b*) Special equipment needed
(*c*) Special chemicals needed
(*d*) Minimum student prerequisite
(*e*) Name and address of director

ANALYTICAL PROJECTS

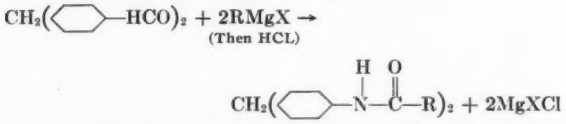
1. *Sensitivity of Inorganic Qualitative Analysis Reagents*
   (*a*) Determine the number of milligrams (in solution) of each of a group of cations required to give a characteristic reaction with 1.0 ml. of each of several different reagent solutions under specified conditions.
   (*b*) Twenty-four small reagent bottles (30–100 ml.) with droppers in the stoppers, or any convenient means of counting the drops of solutions used.
   (*c*) Salts to prepare the cation solutions. Sometimes special organic reagents.
   (*d*) Completion of a course in systematic qualitative analysis.
   (*e*) W. P. Cortelyou, Roosevelt University, Chicago 5, Illinois.
2. *The Magnitude of Some Simple Quantitative Technique Errors*
   (*a*) Is it necessary to grease the lid of a desiccator?
   (*b*) Usual instruments and equipment needed for gravimetric quantitative analyses.
   (*d*) Quantitative analysis.
   (*e*) Ethaline Cortelyou, Department of Chemistry and Chemical Engineering, Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Illinois.
3. *Classification of Cations Based on Qualitative Chromatographic Separation by Means of Specific Solvents*
   (*a*) Determine the R_f values for a group of cations employing as solvents specified mixtures of two alcohols diluted with (*a*) water and (*b*) acetic acid. Keep temperature, cation concentration, and development time constant.
   (*b*) Sheets and rolls of Whatman filter paper prepared for paper chromatography. Wide-mouthed jars or bottles, 12 to 15 inches tall, are useful.
   (*c*) Salts to prepare cations. Solvent solutions, *e. g.*, acetic acid, sulfuric acid, butanol, isopropanol, and other alcohols, if desired.
   (*d*) General chemistry and some qualitative analysis.
   (*e*) Sister Alice Marie, Associate Professor of Chemistry, Mount St. Mary's College, Los Angeles 49, California.
4. *The Development of Quantitative Volumetric Determination of Paint Pigment Constituents*
   (*a*) Comparison of five assigned internal indicators for the titration of zinc.
   (*c*) Special indicators assigned.
   (*d*) Quantitative analysis.
   (*e*) Clovis Adams, The Sherwin-Williams Company, 115th Street and Cottage Grove Avenue, Chicago, Illinois.
5. *The Detection of Ions by Differential Diffusion*
   (*a*) To devise methods for detecting the presence of anions and cations by their different rates of diffusion in gelatinous media, such as concentrated gels of gelatine or polyalcohols.
   (*b*) Petri dishes, watch glasses, and reagent bottles with droppers in the stoppers.
   (*c*) Salts to prepare ionic solutions and developers; also organic reagents.
   (*d*) General chemistry and qualitative analysis.
   (*e*) Marvin Antelman, Research Director, Marantes Laboratories, 7 South Cambridge Avenue, Ventnor City, New Jersey.

INORGANIC PROJECTS

6. *Solubilities of Inorganic Sulfamates in Water*
   (*a*) Determination of the solubility of barium sulfamate in water at 20°, 30°, 40°, and 50°C.; includes preparation and purification of the barium sulfamate.
   (*b*) Screw-capped bottles of approximately 125-ml. capacity; suitable shaking device for six or eight bottles in a thermostat.
   (*c*) Reagent grade sulfamic acid.
   (*d*) Good background in quantitative analysis.
   (*e*) Sister Agnes Ann, Immaculate Heart College, Los Angeles 27, California.
7. *Solubilities of Inorganic Fluoride Salts in Organic Solvents*
   (*a*) Determination of solubility of potassium fluoride in dioxane at several temperatures.
   (*b*) Constant-temperature bath; containers not affected by compounds used, probably polyethylene bottles.
   (*c*) The inorganic fluoride and the organic solvent used.
   (*d*) Elementary quantitative analysis and elementary organic chemistry.
   (*e*) John H. Walkup, Centre College, Danville, Kentucky.
8. *Solubilities of Inorganic Halides (other than Fluorides) in Organic Solvents*
   (*a*) Determination of solubility of lithium bromide in *n*-butyl alcohol at 0°, 25°, and 100°C.
   (*b*) Constant-temperature bath; screw-capped glass bottles of approximately 100–125 ml. capacity; shaking device.
   (*c*) None other than good grade solvent and solute.
   (*d*) One quarter of quantitative analysis or at least be pursuing same.
   (*e*) Kirby E. Jackson, University of Alabama, University, Alabama.

ORGANIC PROJECTS

9. *Preparation and Characterization of Diamides from Methylene Bis-(4-phenyl isocyanate) and Alkyl or Aryl Bromides through the Grignard Reaction:*



   (*a*) Condensation of the RMgX compounds of three or four alkyl or aryl bromides with methylene bis-(4-phenyl isocyanate) and subsequent hydrolysis to the diamide, methylene bis-(*p*-acyl aniline). The purification of the diamides and determination of physical constants.
   (*b*) Two-neck, round-bottomed flasks.
   (*c*) Methylene bis-(4-phenyl isocyanate), alkyl or aryl bromides, metallic magnesium for Grignard reagents, dry ether.
   (*d*) Elementary organic chemistry.
   (*e*) Roy G. Bossert, Ohio Wesleyan University, Delaware, Ohio.
10. *Preparation and Properties of Acylacenaphthenes*
   (*a*) Preparation and properties of 5-(*p*-toluyl)-acenaphthene.
   (*b*) General organic laboratory equipment.
   (*c*) Acenaphthene, *p*-toluyl chloride, carbon disulfide, hydroxylamine hydrochloride, phenylhydrazine hydrochloride, etc.
   (*d*) Organic chemistry.
   (*e*) Edith J. H. Chu, Immaculate Heart College, Los Angeles 27, California.
11. *Characterization of Amines as Salts of Oxalic Acid*
   (*a*) Preparation and crystallization of desired salts and determination of melting points of these derivatives.
   (*b*) Good standard thermometer.
   (*c*) Primary amines.
   (*d*) Two semesters of organic chemistry and preferably a course in qualitative organic chemistry.
   (*e*) Harry Cohen, Roosevelt University, Chicago 5, Illinois.
12. *Preparation of Certain Schiff Bases and Their Reduction with Lithium Aluminum Hydride*
   (*a*) Synthesis of octadecylbenzylideneamine and reduction to N-octadecylbenzylamine.
   (*b*) Three-neck flask, mechanical stirrer, Claisen flask, and, for most preparations, a vacuum pump.
   (*c*) Lithium aluminum hydride.
   (*d*) Elementary organic chemistry.
   (*e*) Bertin L. Emling, St. Vincent College, Latrobe, Pennsylvania.
13. *The Reaction of Alcohols with Activated Aryl Halides*
   (*a*) The product of an alcohol, 2,4-dinitrofluorobenzene, and a tertiary amine catalyst is isolated and purified. The melting point is the physical property sought.
   (*b*) Ordinary laboratory apparatus.
   (*c*) A series of alcohols and 2,4-dinitrofluorobenzene (Eastman or Matheson).
   (*d*) Organic chemistry.
   (*e*) John D. Reinheimer, The College of Wooster, Wooster, Ohio.
14. *Synthesis of Polynuclear Thiophene Compounds*
   (*a*) Synthesis of 2,5-dimethylbenzothiophene.
   (*b*) Standard organic equipment, such as vacuum pump, chemical stirrer, and three-neck flask.
   (*c*) *p*-Thiocresol, lithium metal, chloroacetaldehyde, diethylacetal, and dimethyl sulfate.
   (*d*) Organic chemistry.
   (*e*) F. G. Bordwell, Chemistry Department, Northwestern University, Evanston, Illinois.

PHYSICAL PROJECTS

15. *Determination of Refractive Indexes of Binary Liquid Mixtures at Various Concentrations and Various Temperatures*
   (*a*) Determination of refractive indexes of dioxane-ethylene glycol solutions of various concentrations at some given temperature.
   (*b*) Good refractometer, constant-temperature water bath, circulating pump.
   (*c*) The liquids to be used.
   (*d*) Elementary quantitative analysis and elementary organic chemistry.
   (*e*) R. I. Rush, Centre College, Danville, Kentucky.
16. *Binary Azeotropes to Members of Hydrocarbon Homologous Series with Glycol Ethers*
   (*a*) Study of the vapor-liquid equilibrium compositions as a function of boiling temperature for azeotropic agent with one or more pure hydrocarbon homologues.
   (*b*) Efficient fractionation column, Abbe refractometer, manostat desirable but not necessary.
   (*c*) Carefully purified liquids.
   (*d*) Physical chemistry taken concurrently.
   (*e*) William F. Kieffer, The College of Wooster, Wooster, Ohio.
17. *Determination of Ternary Azeotropes Containing Water and Amines and/or Alcohols*
   (*a*) Investigation of toluene, methyl cellosolve, and ethyl alcohol system.
   (*c*) Carefully purified liquids of the particular system studied.
   (*d*) Physical chemistry taken concurrently.
   (*e*) H. E. Weissler, Incarnate Word College, San Antonio, Texas.
18. *Determination of the Reliability of Ideal Laws in Typical Practical Circumstances*
   (*a*) Determination of the molecular weight of naphthalene from its freezing-point depression in benzene at several concentrations to observe departure from ideality as a function of concentration.

(*d*) Physical chemistry.
(*e*) Nathan Yagol, Roosevelt University, Chicago 5, Illinois.

19. *Chemical Means of Cleaning Ultramicro Pipets*
(*e*) George F. Hand, State Microscopical Society of Illinois, 7512 Olcott Avenue, Hammond, Indiana.

Each of the 19 National Project Directors directs the research on his project by issuing assignment sheets to each student participant through the student's teacher, a Local Project Director. Each project is subdivided into assignments, or research units; each assignment usually requires about 50 hours of work for completion of any library search needed, the laboratory work, and a research report.

Ordinarily the same assignment is made to two or more students, independent of and unknown to each other, in different schools. Each student works under the direct supervision of his own teacher. When a teacher decides a student has completed an assignment, he supervises the preparation of a research report to be submitted to the National Project Director.

Each National Project Director sets his own criteria for accepting or rejecting a report; often acceptance is based upon the checking of results obtained by two or more students. A Certificate of Acceptance is awarded to each student submitting an acceptable report. Each certificate is signed by the student's teacher, the National Project Director, and by the president and secretary of Handbook Publishers, Inc., which furnishes the certificates.

Suitable data may be selected for publication in the "Handbook of Chemistry." A National Project Director may publish data obtained on one or more assignments as a paper, giving full credit to participating students, teachers, and schools. One NaCUR project has been completed and the results were published.[1] Several students have reported their results in papers before student groups of the A. C. S. and of state academies of science. On January 31, 1954, students of Sister Mary Louis of Notre Dame College in Baltimore discussed four NaCUR projects on a college television program.

The program was originally organized at the St. Louis American Chemical Society meetings in 1948 to stimulate undergraduate research and to supply chemical data. It has also served as a stimulant to teachers in small schools who have previously felt their research efforts were handicapped by limited funds, facilities, time, and research quality students. By sponsoring a NaCUR project, a teacher may direct the activities of many students with the assistance of other teachers and the research equipment of several schools.

In addition, the program offers industry an excellent opportunity to cooperate with college teachers in stimulating student interest in chemical careers. In the past, industrial and research foundation chemists have given invaluable aid by suggesting projects. Their daily use of chemical data often means they are better informed than the average chemistry teacher on both the validity and availability of data in many fields.

Sometimes in the pursuit of a large research problem missing bits of data, such as physical constants, must be determined, but these results are not published. No doubt many industrial chemists have tucked away in their notebooks some of the data sought in the 19 current projects. The project directors would appreciate receiving any such data to use in evaluating student results.

The donation of unusual or pure chemicals to be supplied to students studying them is another form of industrial aid that would be most welcome. Many of the participating schools have limited budgets, and the purification of chemicals is so time-consuming that a student seldom can purify a chemical and have much of his 50 hours left for research. Better checks would be obtained if all students working in a chemical had samples from the same source.

The chemistry departments of most small liberal-arts colleges operate on very limited budgets so that they are seldom able to purchase the latest scientific instruments. Many industries, on the other hand, are able to replace adequate equipment with the latest advances in more efficient and more accurate instruments to speed up the solution of their problem. Almost any industry can find a school nearby that would be more than grateful for donations of laboratory equipment that has been replaced by newer models.

Many large companies support graduate fellowships for research in fields of interest to them. A much smaller financial donation would help a school participate in one of the program projects.

Any project suggestions for the 1956–57 NaCUR list would be appreciated very much. Any chemist suggesting a project may decide for himself how much aid he wishes to give on it; he may want to:

(1) Do nothing more than suggest the project.
(2) Explain the reason for suggesting the project and the possible applications of any data obtained.
(3) Outline previous research in the field.
(4) Suggest the procedure and methods to be followed.
(5) Act as consultant.
(6) Direct the project himself.

Any teacher or industrial chemist interested in directing a new project should write to one of the authors as soon as possible, since a project is listed under the direction of the first person to request it. An outline of a project for the 1956–57 school term must be sent to the authors by January 10, 1956.

[1] EMLING, BERTIN, "Some alkyl benzenesulfonates," *J. Am. Chem. Soc.*, **74**, 4702–4 (1952).

SIZE GRADING AND ANALYSIS

R. S. YOUNG
International Nickel Company of Canada, Ltd.,
New York, N. Y.

A DEMONSTRATION of the preparation of a sample for chemical analysis is often included in courses designed for students in mining and metallurgy, but is frequently omitted in a laboratory course in general quantitative analysis. Size grading is an important subject in chemical engineering, but a practical demonstration may not be encountered by the student in his elementary courses. It is possible, however, with very little complication in equipment or time, to introduce to classes in quantitative analysis the important concepts of sample preparation and size grading. These operations may be performed by students in groups, while each student would carry out individually the normal analytical work on a sample. Although all students would determine the same constituent, they might not all have the same sample. Some would work on a representative portion taken before the separation into various sizes by sieving, whereas other students could analyze the sized fractions. The exercise is quite flexible and may be used for the analysis of any common element. Although almost any material can be employed for this experiment, it may be most convenient to carry out the demonstration in courses of quantitative inorganic analysis where such elements as copper, lead, zinc, sulphur, etc., are determined.

Complete instructions, often with accompanying photographs for the sampling of such materials as coal, are given in publications of organizations like the American Society for Testing Materials.[1] Bugbee[2] discusses in some detail various procedures for sampling ores. The student should refer fully to such literature, but it is usually impractical to carry through in an educational laboratory all the steps required to obtain an analytical sample from a large mass of coarse ore. The basic principles can be readily demonstrated on a few pounds of a mill feed or ore varying in Tyler mesh size from about 6- to 325-mesh, obtainable from any mining company. Alternatively, mix half a pound of flotation concentrate or finely-ground high-grade mineral specimen with several pounds of fine gravel and sand ranging from about 6- to 65-mesh. With a set of Tyler screens including meshes 6, 10, 14, 28, 35, 48, 65, 100, 200, 325, and a small riffle or sample splitter, the class may carry out the exercise described here.

If desired, the classic technique of "coning-and-quartering" to reduce a bulk sample to one suitable for analysis can be illustrated with this material, which should have a convenient weight of several kilos. In industrial practice, however, the entire original sample of coarse material is usually crushed to a size convenient for riffling, split down by this means to a small bulk which is ground in a pulverizer, riffled again to provide the final sample which is all passed through a fine sieve and thoroughly mixed, ready for the laboratory. For demonstration purposes it will be sufficient first to mix our material, which has no coarse lumps, by shoveling it into a cone half a dozen times. Then pass it through a riffle as many times as is necessary to reduce the final representative sample portion to about 75 grams, retaining the rejected portions for work to be described later.

Grind this representative sample with a mortar and pestle or a mechanical pulverizer until it all passes through a 200-mesh sieve. Mix very thoroughly by rolling several dozen times on a large sheet of paper, by successive conings, or by a mechanical mixer, and place in a labeled, stoppered bottle. If the sampling has been properly carried out this portion will not only be thoroughly representative of the original lot, but replicate 0.5-g. portions weighed out for analysis should check within recognized limits for the element in question and the procedure used. Some members of the class can analyze this sample in duplicate or triplicate.

It might be mentioned here that the correct technique for completely mixing powdered solids by rolling on paper or thin rubber cloth is too often unknown by those in charge of process control. The writer has seen university graduates preparing a finely-divided solid for analysis by giving it a few rolls back and forth on paper, instead of repeatedly rolling it, in turn, from diagonally-opposite corners. Proper rolling practices can be vividly demonstrated to a class by the preparation of a homogeneous powder from equal parts of finely-divided carbon and limestone.

The rejects from successive rifflings of the original material may now be combined, and weighed on a laboratory scale to the nearest 0.1 g. Obtain the size grading of this material by sieving on successively decreasing screen sizes. Hand or mechanical sieving may be used, the principle in both cases being to continue the operation until virtually no more material passes through. Weigh each size fraction on a laboratory scale or rough balance to the nearest 0.1 g., mix each portion separately by rolling thoroughly on paper, and retain in a sample bottle. The total weight of the sized fractions, of course, should check the original weight of the sample.

These size fractions may be utilized for two purposes:

[1] A.S.T.M., "The Sampling of Coal," A.S.T.M. Standards, 1918, pp. 673–9.

[2] BUGBEE, E. E., "A Textbook of Fire Assaying," John Wiley & Sons, Inc., New York, 1940.

(1) Analysis of 0.5-g. duplicates taken directly from the coarsest and finest fractions as they occurred in the original material will show the student how important is the need for proper size reduction prior to analysis.

(2) After the small portions required for (1) have been withdrawn, reduce in particle size all fractions separately to pass a 200-mesh sieve, thoroughly mix each portion by rolling on paper or rubber cloth, and replace in bottles. Duplicate 0.5-g. samples of these can now be analyzed to give the distribution of the desired element in the particle sizes of the original material. In industrial practice, when a sample must be prepared to pass through a given mesh size, the operation is often accelerated by gentle brushing or the use of one or two steel washers with the sample on the sieve. These aids must be used with due caution, however, to avoid damage to the screen.

Theoretically, it is not strictly correct to withdraw two 0.5-g. samples from the coarsest size fraction in (1) before the latter has been reduced in size to pass a 200-mesh screen, unless the weight of the coarsest size fraction is very large. Otherwise, even with particles minus 6 + 10-mesh in size, the portion withdrawn may differ slightly in composition from the remainder of the sample. For most practical purposes, however, where the coarsest fraction has a weight many times that of the two 0.5-g. samples, it will suffice to assume that the remainder of the coarsest sample, analyzed after the size reduction of (2), is representative of the entire original coarse fraction.

It is informative to include in this exercise a device much used in industrial analysis to minimize sampling errors on heterogeneous substances difficult to reduce in size; this consists of increasing the size of the sample to the point where it is considered representative of the bulk of the material, bringing the sample into solution by appropriate means, making up to a known volume, and withdrawing a suitable aliquot for the actual analytical determination.[3] One may well illustrate the effect of this practice by collecting a quantity of coarse, heterogeneous ore, say minus 6 + 10-mesh, and after mixing as well as possible by rolling, weighing out two 0.5-g. portions for analysis. Then weigh out two 10-g. portions from this same mixed ore, bring into solution, make up to one liter, and withdraw a 50-ml. aliquot from each flask for analysis to compare with the 0.5-g. portions weighed directly.

The analyses for all the determinations suggested above can be distributed among the class, and the results compiled in a recitation period. The concept of weight percentage and weighted averages can be introduced at this stage, and all students should summarize the class results in their laboratory notebooks to show:

(1) Weight of size fractions.
(2) Percentage of size fractions.
(3) Analytical result for each size fraction.
(4) Percentage distribution of the element in various fractions.
(5) Comparison of calculated weighted average of all screen sizes with actual analytical result on the representative sample portion.
(6) Comparison of analytical results on 0.5-g. duplicates of coarsest fraction before grinding through 200-mesh, with those of finest fraction.
(7) Comparison of 0.5-g. duplicates of a coarse product with 50-ml. aliquots from two 10-g. samples of the same size fraction dissolved and made up to one liter.

The table gives an actual example of the results obtained with a copper ore on an exercise of this type.

The calculated weighted average should check closely the percentage of the element obtained from the actual analysis of the representative portion secured initially by riffling the entire sample. The agreement should be within two per cent, *e. g.*, 1.50 and 1.53 per cent, and will usually be well within this tolerance. The effect of decreasing particle size and of increasing sample size in reducing the spread of analytical results on duplicate samples, illustrated in the example above, will be illuminating to the class. Incidentally, it can be pointed out that this procedure of carrying out a size grading,

[3] YOUNG, R. S., "Industrial Inorganic Analysis," John Wiley & Sons, Inc., New York, 1953.

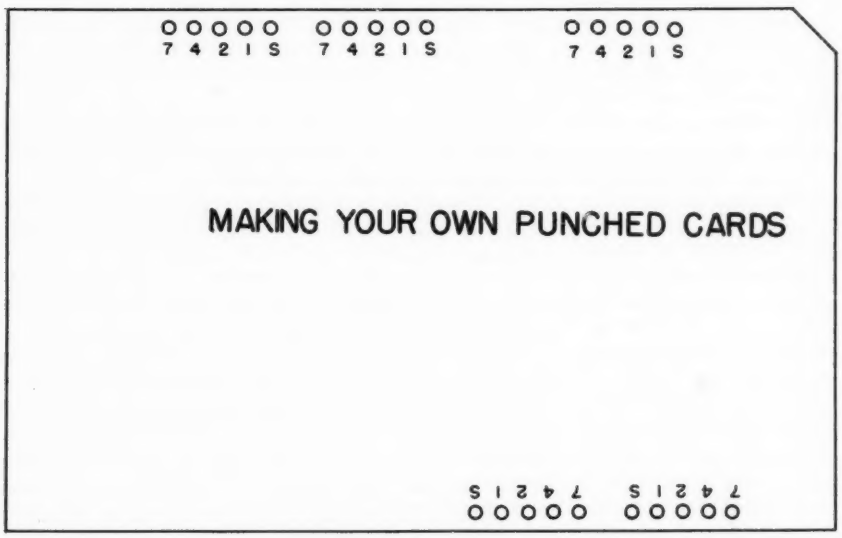
Size fraction (Tyler mesh)	*Wt. of size fraction (g.)*	*% of size fraction*	*Copper (%)*	*Distribution of copper (%)*
Minus 6+10	18.4	0.9	2.15	0.6
Minus 10+14	36.9	1.8	2.33	1.4
Minus 14+28	56.3	2.8	2.46	2.2
Minus 28+35	72.2	3.6	2.67	3.1
Minus 35+48	91.1	4.6	2.78	4.2
Minus 48+65	130.4	6.5	2.92	6.2
Minus 65+100	229.6	11.5	3.01	11.2
Minus 100+200	904.9	45.3	3.08	45.3
Minus 200+325	381.5	19.1	3.39	21.0
Minus 325	78.7	3.9	3.74	4.7

Calculated versus actual results	% Cu	
Calculated weighted average of all screen sizes	3.08	
Analytical result on representative sample portion	3.07	3.08
Effect of size reduction on sample homogeneity		
0.5-g. samples of minus 6+10-mesh	2.28	2.00
0.5-g. samples of minus 325-mesh	3.71	3.77

Effect of sample size on sample homogeneity		
0.5-g. samples of minus 6+10 mesh	2.01	2.30
0.5-g. aliquots from two 10-g. samples of minus 6+10 mesh	2.16	2.12

crushing all size fractions to pass a 200-mesh screen, rolling, and analyzing the individual mesh sizes as well as the representative portion initially cut out from the original material, is one of the best methods of checking the accuracy and precision of any chemical determination and of any laboratory. The original portion may, for instance, be analyzed by two methods to further increase the reliability of this procedure for checking a new method.

The sampling and analytical procedures may also be used to illustrate elementary statistical theories for students of chemistry. Significant figures in weighing size fractions, relation of sample weight to particle size, and scatter of replicates obtained by the class on the original sample and on the various mesh fractions before and after size reduction may all be utilized by the instructor to point out the importance of a sensible statistical approach to laboratory and plant operations.



GEORGE M. BEGUN

Oak Ridge National Laboratory, Oak Ridge, Tennessee

SOME years ago I wished to use punched cards to start a file of *Chemical Abstract* references. I found upon investigation that the available cards were considerably more complicated than I needed, and that the cost of cards and equipment was more than I wished to invest. For these reasons and for reasons of convenience, I have been making my own punched cards ever since. The card design illustrated is the one I have been using, although other systems could be used provided the number of holes is not too large.

A master template was first cut from heavy galvanized iron to insure the production of identical cards. This master was cut exactly 5 by 8 inches. The corner was beveled, and holes slightly larger than those desired in the final card were drilled at the positions shown. In making cards, four or five common 5- by 8-inch file cards are lined up behind the master template. The corners of the cards are then cut off with scissors, and a hand punch is rapidly run down the holes, punching through each guide hole in turn. The punch used is a paper punch purchased at the ten cent store. It is important to keep the cards lined up during this operation, and at this point the advantage of using as few holes as possible will become apparent.

The only piece of commercial equipment I have is a notching punch purchased from the McBee Company.[1] In each field any number from 0 to 9 may be punched by combining the digits 7, 4, 2, and 1. If only one punch is required, as for 7, 4, 2, and 1, the *S* hole is also punched out to enable selective sorting of any number desired. Zero is punched by combining 7 and 4. This method of punching is described by Casey,[2] except that a separate zero hole is employed. Numbers up to 999 may be punched along the top edge of the card, and 99 additional on the lower edge. The two fields on the lower edge of the card are quite convenient for an atomic-number classification. Ice picks are efficient as sorters although it is wise to dull the points a bit for safety.

A close examination of what is desired in a filing-system code using punched cards will often show that either a very elaborate system is needed or that a relatively small number of holes will be sufficient. In this latter case it is quite simple to make your own cards. An added advantage of the system is that notes can be taken on any 5- by 8-inch card, and the card can be made into a punched card later without recopying.

[1] The McBee Co., 295 Madison Ave., New York 17, New York.

[2] CASEY, ROBERT S., "Punched Cards," Reinhold Publishing Corp., New York, 1951.

TWO EXPERIMENTS FOR THE RADIOCHEMISTRY LABORATORY

WHITTIE J. McCOOL AND ROBERT R. HENTZ
North Carolina State College, Raleigh, North Carolina

Sulfur^{35} possesses many desirable characteristics for use in the modest student radiochemistry laboratory which has as its primary objective illustration of applications of radionuclides to chemistry. Only soft betas of energy 0.17 m. e. v. and range 35 mg./cm.^{2} in aluminum are emitted by this nuclide. It is suitable for self-absorption studies, yet may be counted conveniently in economical end-window units of window thickness less than 2 mg./cm.^{2}, either in infinitely thin or infinitely thick layers. The softness of the radiation permits handling of all glassware and requires no elaborate shielding precautions or manipulative techniques. The relatively long half-life, 87.1 days, avoids decay corrections for experiments extending over several laboratory periods and makes it possible to order the isotope sufficiently in advance to insure that the desired activity will be available when it is needed. The biological half-life of 22 days and effective half-life of 18 days make sulfur^{35} one of the safer isotopes to work with. The maximum permissible amount in the total body is set at 100 microcuries (*1*). Sulfur^{35} can be obtained from the Atomic Energy Commission in the form of barium sulfide, sulfuric acid, or elemental sulfur. These characteristics make sulfur^{35} a versatile nuclide especially suitable to the more involved chemical experiments in which hazard must be minimized. Two such experiments, developed for the radiochemistry laboratory at North Carolina State College, are described.

PREPARATION OF RADIOACTIVE SULFUR

Sulfur of the desired specific activity must be prepared from the high-specific-activity sulfur received from the A.E.C. in the form of elemental sulfur in benzene solution contained in a glass capsule. The capsule was broken and the contents were transferred to a ground-glass-stoppered 500-ml. bottle using a transfer pipet operated by a hypodermic syringe. The benzene was allowed to evaporate. The radiosulfur was dissolved in 500 ml. of alcohol to which 14 mg. of alcohol-soluble carrier sulfur had been added. The activity per ml. of alcohol was determined by transferring a suitable small volume of the solution with a micropipet to a stainless-steel counting cup, evaporating the alcohol with an infrared lamp, and counting the sulfur deposit as an infinitely thin layer with a thin-window G-M tube. A value of approximately 0.4 μ c./ml. was obtained. Care must be taken to remove the infrared lamp upon achieving dryness, since these small amounts of sulfur gave evidence of being easily oxidized. The sulfur's^{35} radiochemical purity may be checked at this point by half-life and absorption curve measurements.

Sulfur of the desired specific activity was prepared by the taking of aliquots of the alcohol solution of 1 ml. or 5 ml., evaporation of the alcohol, and addition of 5 g. of carbon disulfide-soluble inactive sulfur. The mixture was dissolved in carbon disulfide and evaporated to dryness, leaving a homogeneous sample of radiosulfur. This gave specific activities of 0.08 μ c./g. or 0.4 μ c./g., respectively. The inactive sulfur was made carbon disulfide-soluble by passage of carbon disulfide over flowers of sulfur held in a filter paper and evaporation of the filtrate.

These operations were carried out in a hood and over a stainless-steel tray. A careful survey of the area was made after each operation with a Tracerlab survey meter. Radio materials were not removed from the hood except in a closed container. Glassware was placed in boiling nitric acid until the activity had been reduced to near background. Pipets to be cleaned were placed point down in a Bunsen funnel held in a suction flask by a rubber stopper; successive volumes of nitric acid, hydrochloric acid, water, alcohol, and acetone were added at the top, while aspiration was applied to the system.

EXPERIMENT 1

Voge (*2*) and Andersen (*3*) have shown that there is no exchange of sulfur atoms in the thiosulfate ion. This is easily verified in one three-hour laboratory period by synthesis and decomposition of thiosulfate, if students work in pairs and plan work to utilize waiting periods. Radiosulfur is dissolved in a sodium sulfite solution to form the thiosulfate ion which is then decomposed by acid.

$$S^* + SO_3^{--} = S^*{-}SO_3^{--}$$
$$S^*{-}SO_3^{--} + 2H^+ = S^* + SO_2 + H_2O$$

The sulfur dioxide is collected and precipitated as barium sulfite. The sulfur is coagulated. Zero activity of the barium sulfite fraction indicates nonequivalence of the sulfur atoms in thiosulfate ion. Equivalence of the sulfur atoms would divide the activity equally between the two fractions.

Preparation of a Standard Sulfur Sample. Infinite thickness for the stainless-steel counting cups used corresponded to a uniform layer of mass 170 mg. Experiments were designed to give samples for counting of at least 300 mg. All samples were counted for a time sufficient to reduce the statistical counting error to less than 2 per cent.

A standard sample of sulfur was first prepared by weighing approximately 500 mg. of radiosulfur (0.08

μc./g.) into a stainless-steel counting cup. The sulfur was melted with an infrared lamp to form a uniform layer. After the sample had solidified, it was counted, then melted and counted again to determine the reproducibility of surface conditions. The variation was approximately 2 per cent. Loss in weight was negligible.

Equivalence of Sulfur Atoms in Thiosulfate Ion. Four-hundred milligrams of radiosulfur (0.08 μc./g.) was weighed into a 250-ml. Erlenmeyer flask. The sulfur was dissolved in 20 drops of carbon disulfide and precipitated by addition of 10 ml. of acetone. The acetone was decanted, leaving finely divided sulfur which was washed by decantation with distilled water. To the sulfur, 100 ml. of 0.24 *M* sodium sulfite solution was added. A one-hole rubber stopper with a short glass tube and a split rubber policeman served to permit escape of steam and keep the solution relatively free of oxygen. The solution was boiled for one hour. Since the sulfite was in excess, disappearance of the sulfur indicated completion of reaction.

The Erlenmeyer flask was now connected to a three-hole rubber stopper in a bubbling train. One hole admitted a buret for hydrochloric acid, another a fritted-glass bubbling tube for incoming air, and the third an exit tube to a saturated barium hydroxide solution and an aspirator. A saturated barium hydroxide solution also served to absorb carbon dioxide from the incoming air. Aspiration was applied to the system as hydrochloric acid was added. The thiosulfate was decomposed by addition of 15 ml. of 12 *N* acid leaving the solution about 1 *N* in acid. The buret was then replaced with a thermometer and aspiration was continued as the solution temperature was raised with a low flame. The sulfur dioxide was collected as barium sulfite in the saturated barium hydroxide solution. Elimination of sulfur dioxide was found to be complete in less than an hour at 60–80°C.

TABLE 1
Decomposition of Radiothiosulfate
(Sulfur Standard = 535 c./min.)

S c./min.	*$BaSO_3$ c./min.*
439	0
449	0

To aid coagulation the barium sulfite was placed in a hot-water bath for 30 minutes. The precipitate was washed several times by decantation and the slurry that remained was evaporated to a thick paste with an infrared lamp. Some of the paste was transferred to a counting cup and evaporated to dryness. The sulfur was washed into a beaker where it was washed by decantation and transferred to a counting cup by brushing the sulfur out with a rubber policeman (the work of the policeman is greatly aided by a few drops of water). The sulfur was dried and melted into a uniform layer with the infrared lamp. Table 1 shows the results.

A 92.5 per cent excess of sodium sulfite was used in this experiment to minimize the time required for complete reaction of the sulfur. On the assumption that sulfite does not exchange with thiosulfate under these conditions, the expected activity of the sulfur is 268 c./min. if the sulfur atoms are equivalent. The expected activity of the barium sulfite, less by the isotopic dilution factor and the ratio of the molecular weight of sulfur to that of barium sulfite, is 21 c./min. However, Voge (*2*) reports that the half-time for the sulfite-thiosulfate exchange is less than one hour at 100°C. Equivalence of the sulfur atoms would distribute the activity uniformly through all sulfur in the system if this exchange occurs. The expected activity of the sulfur fraction would be 183 c./min., and that of the barium sulfite fraction would be 27 c./min. The measured zero activity of the barium sulfite fraction and high activity of the sulfur fraction indicate nonequivalence. The sulfur sample had visible contamination with sodium chloride from the reaction medium, which may account for the somewhat lower counting rate compared to the standard. Isotopic dilution may be avoided by preparation of the radiothiosulfate as in Experiment 2. However, little is gained by the extra time and labor required in removal of the excess sulfur by filtration. Equivalence would then give a sulfur activity of 268 c./min. and a barium sulfite activity of 40 c./min.

EXPERIMENT 2

In this experiment, radiothiosulfate prepared as in Experiment 1 is used in the synthesis of sodium tetrathionate with the two central sulfur atoms labeled.

$$2S^*—SO_3^{--} + I_2 = SO_3—S^*—S^*—SO_3^{--} + 2I^-$$

The exchange reaction between radiotetrathionate and inert thiosulfate is then studied.

$$SO_3—S^*—S^*—SO_3^{--} + S—SO_3^{--} = SO_3—S^*—S—SO_3^{--} + S^*—SO_3^{--}$$

The thiosulfate is separated by precipitation as the barium salt, which is counted to determine the per cent exchange.

The polythionates may be represented by the general formula:

$$SO_3—S_x—SO_3^{--}$$

with x taking on values from zero up. For $x = 0$, the compound is known as a dithionate. For x greater than zero, the compounds are named successively tri-, tetra-, penta-, and hexathionate. Foss (*4*) has established that the polythionates contain unbranched sulfur chains. Christiansen (*5*) has shown that the characteristic reaction with sulfite (*6*):

$$SO_3—S—S—SO_3^{--} + S^*O_3^{--} = SO_3—S—S^*O_3^{--} + S_2O_3^{--}$$

proceeds by displacement of the thiosulfate ion by sulfite ion rather than extraction of a sulfur atom. He labeled the sulfite ion as shown and found 97 per cent of the activity in the trithionate ion. He assumed the remaining 3 per cent activity to be present as sulfite owing to slight reversibility of the reaction. Fava (*7*) has studied the exchange between polythionates and

thiosulfate with sulfur[35] and shown an exchange of thiosulfate groups to occur, and not of sulfur atoms.

Synthesis of Radioactive Tetrathionate. To 3 g. of radiosulfur (0.4 μc./g.) 65 ml. of 1.2 *M* sodium sulfite was added, and the solution was boiled for one hour to form thiosulfate as described in Experiment 1. Failure of a precipitate to form when a few drops of solution were added to a 0.4 *M* calcium chloride test solution indicated complete conversion of sulfite ion. The excess sulfur was filtered off and the filtrate evaporated to about 25 ml. Sodium tetrathionate was synthesized by Sander's method (*8*). The thiosulfate solution was added dropwise with stirring to a solution of 11 g. of iodine in 200 ml. of absolute alcohol. The precipitate was allowed to coagulate for five minutes. It was filtered with a Büchner funnel and Whatman No. 42 paper. The tetrathionate was washed with three 10-ml. portions of absolute alcohol and was dried under an infrared lamp to a constant weight of 6.9 g., an estimated yield of 58 per cent. Several batches were synthesized during the course of the work. Yields ranged from 50 to 70 per cent. Iodine titration of a portion of the tetrathionate always yielded less than 5 per cent total reducing agent assumed to be thiosulfate.

Standard Barium Thiosulfate. A variation of the Christiansen reaction was used to prepare a standard barium thiosulfate sample:

$$SO_3\text{—}S^*\text{—}S^*\text{—}SO_3^{--} + S^*O_3^{--} = SO_3\text{—}S^*\text{—}SO_3^{--} + S^*\text{—}SO_3^{--}$$

A 2-g. sample of radiotetrathionate was dissolved in 25 ml. of water and the pH was adjusted to 6. Ten milliliters of 0.4 *M* sodium sulfite was added, and the reaction was allowed to continue for one hour at room temperature. Barium thiosulfate was precipitated by addition of 15 ml. of 1.5 *M* barium chloride. As noted by Fava (*7*), separation as the barium salt requires a thiosulfate concentration of at least 0.05 *M*. At lower concentrations precipitation is slow and incomplete. Separation is never complete because of the moderate solubility of barium thiosulfate. However, the salt is obtained free of polythionates and in ample yield.

A small amount of barium sulfite was also precipitated. Since it was finely divided, almost colloidal, it was largely separated from the well formed thiosulfate crystals in several washings by decantation. The thiosulfate was transferred to a counting cup with a rubber policeman and dried with an infrared lamp. Care was taken not to decompose the sample by over-heating. Dryness was determined by counting the sample, drying, and counting to constant activity.

Thiosulfate-Tetrathionate Exchange Reaction. A 1.8-g. sample of radiotetrathionate was dissolved in 50 ml. of water. The pH was adjusted to about 6, and 50 ml. of 0.27 *M* sodium thiosulfate was added. After a given reaction time, 50 ml. of 1.5 *M* barium chloride was added to precipitate barium thiosulfate which was washed three times by decantation, transferred to a counting cup, dried, and counted as was the standard.

TABLE 2
Exchange Between Tetrathionate and Thiosulfate Ions (Standard BaS_2O_3, 450 c./min.)

Reaction time, min.	0.25	5	45	90
Per cent exchange	81	67	60	61

Exchange experiment data are given in Table 2. The per cent exchange was calculated as the per cent ratio of observed activity to expected activity for complete exchange. Expected activity is given by:

$$A = A_s\,(n^*/n)$$

where A_s is the activity of the standard, n^* is the number of millimoles of labeled thiosulfate groups (twice the number of millimoles of tetrathionate), and n is the total number of millimoles of thiosulfate present in the added thiosulfate ion and in the tetrathionate ion. Sodium tetrathionate dihydrate of molecular weight 306 was assumed to be the form of the tetrathionate.

The conclusion may be drawn that there is a rapid exchange of thiosulfate groups between the thiosulfate and tetrathionate ions at pH 6 and room temperature. An exchange time of one minute or less may be used in the student experiment. Only one experiment was performed at 0.25 minutes. The variation in per cent exchange at the three other times is representative of the reproducibility obtained. Therefore, no conclusion on the apparent time effect is warranted.

The instability of the polythionates and the complexity of their reactions may account for the failure to observe 100 per cent exchange. Decomposition of the polythionates would yield barium-sulfite contamination. A thiosulfate-catalyzed conversion of tetrathionate into pentathionate and trithionate (*6*) may compete with the simple exchange and prevent complete exchange between all nonsulfite sulfur atoms.

Christiansen's result requires that trithionate exchange slowly with thiosulfate, if at all. Because of the difference in bonds involved in this exchange, the activation energies and transition states would be different in the two cases. This may account for the observed difference in rate.

SUMMARY

The experiments have been presented as they were developed to permit a complete discussion of the difficulties encountered, observations made, and results obtained. The presentation given is readily translated into procedural directions for the laboratory.

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(1) National Bureau of Standards, Handbook 52.
(2) Voge, H. H., *J. Am. Chem. Soc.*, **61**, 1032 (1939).
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(4) Foss, O., *Acta. Chem. Scand.*, **4**, 404–15 (1950).
(5) Christiansen, J. A., and W. Drost-Hansen, *Nature*, **164**, 759 (1949).
(6) Göhring, M., W. Heibing, and I. Apple, *Z. anorg. Chem.*, **254**, 185–200 (1947).
(7) Fava, A., *Gazz. chim. ital.*, **83**, 87–97 (1953).
(8) Sander, A., *Z. angew. Chem.*, **28**, No. 1, 273–7 (1915).

A PRECAUTION IN THE USE OF MAGNETIC STIRRERS

MOSES PASSER
University of Minnesota, Duluth, Minnesota

STIRRING bars for magnetic stirrers are available unsealed, or sealed in one of a variety of coatings: glass, Teflon, Kel-F, or a hard thermosetting plastic. Some time ago we carried out a Rast-Soltys camphor molecular-weight determination using vegetable oil in a tall-form beaker as the bath, which was internally heated by a coiled resistance wire and stirred by a magnetic stirrer with a hard-plastic-coated stirring bar. The sample was enclosed in a sealed, thin-walled, melting-point capillary attached to the thermometer. The heating proceeded normally and no unusual phenomena were observed until the temperature reached about 170°C. Then suddenly a violent explosion took place, spattering hot oil onto the face and neck of the operator. (Fortunately, the wearing of safety glasses was a routine requirement in the laboratory, and since the liquid was vegetable oil rather than the sulfuric acid sometimes used, the resulting burns were not permanent.)

The following observations indicate strongly that it was the plastic housing of the stirring bar, rather than the sealed capillary, which exploded:

(1) Only the bottom of the beaker was shattered, and it was sheared off neatly, leaving the cylindrical beaker wall intact.

(2) The plastic housing of the stirring bar was shattered.

(3) The thermometer was not damaged.

(4) Later experiments with the same compound in which Teflon-coated and Kel-F-coated stirring bars were used did not result in explosions.

We would therefore suggest that for high-temperature work in inert solvents only uncoated magnetic stirring bars be used, and where a protective coating is necessary that it be a soft material which will tear rather than shatter when subjected to the high pressures caused by trapped water vapor, air, or other gases.

A. C. S. EXAMINATIONS COMMITTEE ANNOUNCES TWO NEW TESTS THIS YEAR

A NEW examination, Physical Chemistry, Form L, is featured in the national college testing program of the Examinations Committee of the A. C. S. Division of Chemical Education.

Form L is a new test assembled from items submitted and criticized by about 60 collaborators. The selection of questions included is based upon pretesting under classroom conditions in more than 30 institutions and an analysis of the difficulty and reliability of each question. To obtain more extensive coverage of theoretical concepts, questions dealing specifically with laboratory manipulation have been omitted.

This examination covers topics customarily treated in the year's course in physical chemistry. Section I includes gases and kinetic-molecular theory, the liquid and solid states, and laws of solutions. Section II includes the laws of thermodynamics, thermochemistry, free energy, homogeneous and heterogeneous equilibria, and electrochemistry. Section II includes kinetics, atomic and molecular structure, and radioactivity.

Form L is a new test and norms will be established from the results of the 1955 testing program and mailed to participants.

In addition, the General Chemistry, Form K, has been reprinted. The General Chemisty Subcommittee, taking advantage of this printing, has gone further to clarify or improve the wording of some additional items. This will not result in alternation of the rights key. However, in a few items it may result in slightly improved student performance, which will be reflected in the new norms calculated in the summer of 1955. There should be no major problem in using the first and second printings mixed indiscriminately.

These two tests are part of the spring testing program sponsored by the Examinations Committee. In the program the following tests are featured:

General Chemistry: Form Z, Form G, Form K (new test);
Qualitative Analysis: Form Y, Form H, Qual. Supplement Form J;
Quantitative Analysis: Form Y, Form G;
Organic Chemistry: Form Y, Form H;
Biochemistry: Form X, Form Z, Form K;
Physical Chemistry: Form L (new test).

Further information and copies of the tests may be obtained from Dr. Theo. A. Ashford, Committee Chairman, St. Louis University, St. Louis 4, Missouri. Limited copies of older examinations are available in addition to the tests featured in the testing program.

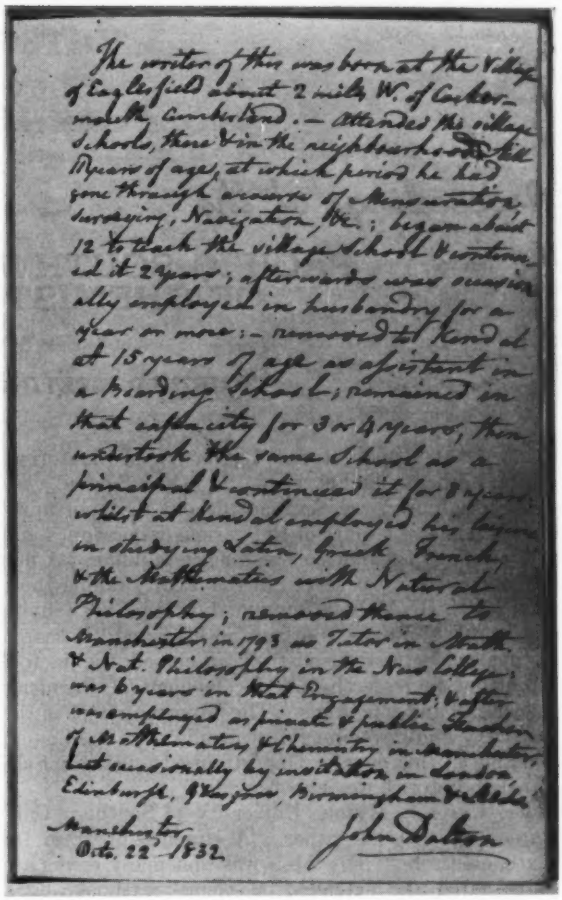
The Examinations Committee Testing Program has shown much growth in recent years. More than 48,000 students in 550 colleges and universities in the United States and several foreign countries were tested under this program last year. Many more are expected to participate this year with the publication of the new tests.

JOHN DALTON'S "AUTOBIOGRAPHY"

DENIS I. DUVEEN
New York, New York

HERBERT S. KLICKSTEIN
The Johns Hopkins University, Institute of the History of Medicine, Baltimore, Maryland

JOHN DALTON (1766–1844), one of the leading protagonists of the atomic theory, has been the subject of a number of full-length studies;[1] Dalton himself, however, left no extensive personal memoirs so that these are based on other sources. It is, therefore, of some interest to learn that Dalton penned a short autobiographical sketch on at least two occasions. The first was written on October 22, 1832 (Manchester) when Dalton was 66 years of age, and was presented to Richard Roberts (1789–1864), the Manchester inventor, who was then making an extensive autograph collection of famous personages of his time. Roberts included the sketch in his "Book of Autographs."[2] It was reprinted from this source in the first full biography of Dalton by Henry, published just 100 years ago.[3] The original manuscript volume of the "Book of Autographs" has recently come into the possession of one of the present authors (Duveen); the Dalton autobiography is bound in as the first item[4] and is here reproduced as a photograph from this source. The text of the manuscript copy differs from the printed version referred to in some details of punctuation, in the use of "&" instead of "and," in the employment of upper-case letters, and in extensive use of abbreviations which are given in full in the printed text. The written copy also includes "Manchester" above the date, which is omitted in the printed transcription. It is noteworthy that Dalton's autobiography has but 172 words and is characterized by the simplicity and straightforwardness so typical of its author. The full text from the manuscript follows.


The writer of this was born at the Village of Eaglesfield about 2 miles W. of Cockermouth Cumberland.— Attended the village Schools, there & in the neighbourhood till 12 years of age, at which period he had gone through a course of Mensuration, Surveying, Navigation &c.; began about 12 to teach the village School & continued it 2 years; afterwards was occasionally employed in husbandry for a year or more;— removed to Kendal at 15 years of age as assistant in a Boarding School; remained in that capacity for 3 or 4 years, then undertook the same School as a principal & continued it for 8 years, whilst at Kendal employed his leisure in studying Latin, Greek, French & the Mathematics with Natural Philosophy; removed thence to Manchester in 1793 as Tutor in Math. & Nat. Philosophy in the New College, was 6 years in that Engagement; & after was employed as private & public Teacher of Mathematics & Chemistry in Manchester, but occasionally by invitation in London, Edinburgh, Glasgow, Birmingham & Leeds.
Manchester
Oct. 22 1832
John Dalton

The writer of this was born at the Village of Eaglesfield about 2 miles W. of Cockermouth, Cumberland.—Attended the village

[1] HENRY, W. C., "Memoirs of the Life and Scientific Researches of John Dalton," London, 1854; A. R. SMITH, "Memoir of John Dalton, and History of the Atomic Theory up to His Time," London, 1856; H. LONSDALE, "John Dalton," London, 1874; H. E. ROSCOE, "John Dalton and the Rise of Modern Chemistry," New York, 1895; H. E. ROSCOE, "A New View of the Origin of Dalton's Atomic Theory; A Contribution to Chemical History, Together with Letters and Documents Concerning the Life and Labours of John Dalton," London, 1896; J. P. MILLINGTON, "John Dalton," London, 1906; L. J. NEVILLE-POLLEY, "John Dalton," London, 1920; E. M. BROCKBANK, "John Dalton, Some Unpublished Letters of Personal and Scientific Interest with Additional Information About His Colour-vision and Atomic Theories," Manchester, 1944.

[2] This manuscript apparently was never published.

[3] HENRY, W. C., *op. cit.*, p. 2.

[4] The original manuscript "Book of Autographs" is a small octavo volume of 75 leaves without title-page, bound in contemporary brown calf. The first leaf is blank, then follow 40 entries (some of several pages) on 52 recto and one verso page, 22 blank pages, and one leaf with an incomplete index, probably in Roberts' hand. Among the persons who wrote into the book during the years 1832–41, the following may be mentioned here: John Dalton, William Henry, N. Paganini, David Cox (with full-page watercolor), John Murray, Peter Barlow, Charles Babbage, John Phillips, Heinrich Rose, Edward Turner, Wilhelm K. Röntgen, David Brewster, Charles Wheatstone, Justus Liebig, Wm. Edward Parry, Alexander Mitchell. Laid in on a separate sheet is a short autograph, signed message of Napoleon III.

Schools, there & in the neighbourhood, till 11 years of age, at which period he had gone through a course of Mensuration, Surveying, Navigation &c.; began about 12 to teach the village School & continued it 2 years; afterwards was occasionally employed in husbandry for a year or more:—removed to Kendal at 15 years of age as assistant in a Boarding School; remained in that capacity for 3 or 4 years, then undertook the same School as a principal & continued it for 8 years; whilst at Kendal employed his leisure in studying Latin, Greek, French, & the Mathematics with Natural Philosophy; removed thence to Manchester in 1793 as Tutor in Math. & Nat. Philosophy in the New College: was 6 years in that Engagement; & after was employed as private & public Teacher of Mathematics & Chemistry in Manchester, but occasionally by invitation in London, Edinburgh, Glasgow, Birmingham & Leeds.

John Dalton

Manchester,
Octo. 22—1832.

The second autobiographical summary that Dalton wrote was inscribed to Miss Catherine Johns, the daughter of the family with whom Dalton boarded for 26 years (1805–30).[5] This later sketch was written on February 19, 1833, and is almost identical with the 1832 version with the exception of some minor changes. This suggests that Dalton must have kept a fair copy of his earlier outline and copied directly from it; he may also have made other copies, although none has come to light. The 1833 manuscript is reproduced as a facsimile folding plate in the works of both Henry and Roscoe (1895).[1]

[5] Miss Johns has left some interesting notes on Dalton's personal habits; these are quoted in the various biographies listed above.

Proceedings of the

PACIFIC SOUTHWEST ASSOCIATION OF CHEMISTRY TEACHERS

COMBINED MEETING AT SANTA BARBARA

THE PSACT met at the University of California, Santa Barbara, on February 12, 1955. Several very interesting papers were presented, and an opportunity was provided for tours of the various laboratories and classrooms of the new college science building. A fine buffet luncheon was served in the faculty dining room after which Dr. Melville Sahyun, director of the Sahyun Laboratories of Santa Barbara, in his paper "Research in pharmaceutical chemistry," discussed the factors important in research and development of chemicals into useful and safe drugs. The important steps in the discovery and development of insulin were used as an example in this paper. Opportunity to visit the Sahyun Laboratories was also provided.

Dr. Karol J. Mysels, University of Southern California, entitled his paper, "A dragnet program for textbook errors." His thesis was that many errors are perpetuated and extended in science textbooks by a chain-reaction type of process wherein a student learns from a teacher or textbook, and in turn teaches and writes textbooks. Since an author must lean so heavily on other authors and teachers, errors are undetected and perpetuated. Several examples were given, including the common statement in freshman chemistry texts that gases are less soluble in liquids at high temperature than at low temperature; actually many gases show increases in solubility as temperature increases.

Dr. Mysels proposes to stop the perpetuation of this type of error by conducting a clearinghouse for the corrections. Scientists who discover errors in textbooks are to inform Dr. Mysels of the error, the correct facts, and the references to the original works that established the facts. After being carefully checked, the information will be published in THIS JOURNAL. In this way it is hoped that widespread bits of misinformation will be gradually eliminated from texts.

Dr. James N. Pitts, University of California, Riverside, presented a paper entitled "Recent chemical techniques for micro and semimicro analysis of gases." He described the Blacet-Leighton apparatus for micro gas analysis, showing the operation of the actual equipment and explaining its use with the help of slides. Dr. Pitts also showed and described a simple, low-priced variation of the apparatus, suitable for use by students in advanced quantitative analysis classes.

The third morning paper, presented by Drs. Donald R. Hogg and David Peters, Queen Mary College, University of London, was entitled "The training of chemists in England." The doctors, both doing research work at the University of Southern California, compared the highly specialized, intensive, government supported training available to a small per cent of English students to the broader, less specialized American training which is available to more students.

Open house was held Friday evening at the home of Professor and Mrs. Webb for those who arrived in Santa Barbara the day before the main meeting.

Report of the

NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS

THE TEACHER AND MODERN CONCEPTS IN INORGANIC CHEMISTRY[1]

RAYMOND E. KIRK
Polytechnic Institute of Brooklyn, Brooklyn, New York

One who presumes to speak to this group should, it seems to me, start by disclaiming any special expertness either in the subject matter of chemistry or in the many excellent ways by which young people are brought to an understanding and an appreciation of our science. Perhaps, however, the fact that I have attempted to teach chemistry at the level of the first course in college for forty years makes it likely that I have made as many and as varied mistakes as anyone here present. As one who has long claimed some small measure of specialization in the field of inorganic chemistry, perhaps I may also be permitted to comment on how the modern concepts of chemistry have aided us as teachers in making clearer and therefore more attractive this division of our discipline. I have also had some reason to note the need of this same use of modern concepts in the field of chemical technology.

I must at once make clear that I would never confine the first course in chemistry in either school or college to the facts of inorganic chemistry. I share the view now, I believe, generally adopted that the first course must be one that draws from all fields of chemistry, pure and applied. What I shall discuss in one subject-matter field of chemistry is, of course, possible of extension to other fields.

We are finding that the many and diverse facts from chemical experience may be presented in a simpler and logical fashion if we discard certain of the erroneous though traditional methods of presentation and representation. In many instances these practices were justified when they were started, in other instances they were based on misinformation or ignorance or both. It seems to me that some of them were based on carelessness or even on slovenliness. Let us seek a few illustrations.

One of the basic ideas of chemistry is the concept of the reactive particle in chemical change. In the very early days of the science one had, perforce, to make arbitrary assumptions regarding the complexity (or lack of complexity) of the reactive particles. Today we are often amazed to discover how nearly correct many of these assumptions were. In other instances, they have been very incorrect. There are more such cases among inorganic compounds than among organic ones. In a few cases these incorrect ideas have persisted to confuse the unwary mind.

When Josiah Parsons Cooke, of Harvard, wrote his once famous textbook called "The New Chemistry" he stressed the certainties regarding the complexity of the molecules of many substances that had resulted from the use of the ideas of Avogadro and of Cannizzaro. Indeed, that was the reason for his title. We use the same arguments today and our students are thrilled by their clarity and their elegance. But Cooke was equally careful to note the limitations of these methods and to stress the large number of substances whose molecular complexities were still unknown. Cooke must have been a magnificent teacher, for the faded pages of his text reveal that in each and every instance where the molecular complexity was not known he placed a bracket around the formula. Thus, he wrote CO_2, or HCl, since these molecules had been established as entities.

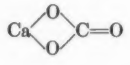
However, [NaCl] or [Na_2O] meant that there was no evidence at hand by which one could establish the complexities of the particles assumed to be present. Would that all of those who followed Cooke had been as meticulous. Even today one sometimes encounters a freshman student in an institute of technology who believes firmly in the diatomic molecule of sodium chloride in the solid state. Fortunately, we now have the experimental evidence at hand concerning the discrete character of sodium ions and chloride ions in the solid state. Unfortunately, we still do not have a generally accepted way by which the student may be warned

[1] Presented at the Sixteenth Summer Conference of the NEACT, University of Massachusetts, Amherst, Mass., August 20, 1954.

that the formulas CO_2 and NaCl are to be interpreted in very different fashion! This should not prevent us from stressing the differences in our teaching.

The tremendous success of "The New Chemistry" at just the time of the tremendous growth of organic chemistry gave great impetus to the idea of writing formulas, many of which were based on certain knowledge and therefore meant something very specific about molecular complexities. However, the methodology of the first course in chemistry sometimes suffered. The first course was at that time almost certain to be taught by a distinguished chemist whose first love was organic chemistry. There was a fatal temptation to extrapolate from the relatively certain molecular situation in organic chemistry and thus arrive at dogmatic ideas about molecules of inorganic substances—ideas that now seem to have been very fantastic.

My first instruction in chemistry, by a magnificent teacher, left me with the idea that calcium carbonate was a discrete pentatomic molecule, where carbon had its "four valences" distributed in such a fashion that one oxygen atom was related to the carbon atoms in a manner very different from the other two oxygen atoms, since these were involved in tying the atoms of calcium to the carbon.



As a student preparing for the university, I was completely satisfied! I am sure that the professors of the university would have shared my satisfaction. Each one of you could expand my illustrations.

In similar fashion, the formula K_2SO_4 may be as misleading as was the older formula for the same substance, $K_2O{\cdot}SO_3$. Whether we are dealing with the solid or with a water solution, we can now bring to the discussion additional evidence regarding the likely particles and their likely structure. The very complexity of hydration effects with potassium cations should make this a very challenging bit of subject matter.

The complexity of hydration of cations has sometimes been cited as an argument in favor of the neglect of hydration in the writing of the formulas of ions in solution. This, it seems to me, is an ostrich solution.

Fortunately, evidence is now available in a rapidly increasing number of cases which establishes beyond reasonable doubt the complexity of the dominant ionic species in usual concentrations. Thus, for example, $Cu(H_2O)_4^{++}$ is as certainly established as the dominant ionic species as is $Cu(NH_3)_4^{++}$, and by the same methods. It is a matter of great satisfaction that an increasingly large number of writers of elementary texts are willing to face up to the "facts of life" in this respect.

It is also now generally recognized that one may best understand the reactions of hydrogen ions in solution by recognizing as a reality the great tendency of the proton to solvate. I am at a loss to understand why there still persists, in many quarters, such stubborn resistance toward writing the formula H_3O^+ in recognition of the dominant cationic species in water solutions of acids.

Shortly after I came to my present teaching post, more than twenty years ago, an instructor in the department was asked, "What about the new professor from the West?" The answer was, so I am told, "Oh, he is a crazy radical! He even thinks that hydrogen ions are wet!" I am sure that he was equally critical of my suggestion to my classes that the action involved when hydrogen chloride gas was allowed to come in contact with water met the usual criteria cited by our textbook for "a chemical change." New molecular species had appeared! Believe it or not, we still find that some of our first-year teaching fellows (from institutions where the department has been approved by the A. C. S.) share the confusion of that instructor. (Incidentally, he is now earning a salary in industry that seems extremely large to an academic man!)

Another practice that has often confused students and teachers alike is that of using formulas as convenient shorthand symbols with little if any warning that these formulas may or may not conform with the known facts regarding the particles that are actually present. Thus, we talk about the "qualitative analysis of the *cations*," and write, perhaps, "the separation of Cu^{++} and As^{+5}." Neither of these formulas represents the dominant ionic species involved. The student is asked, "How does one separate Cu^{++} and Cd^{++}?" Or he is instructed to "separate As^{+5} from Sb^{+5}."

Yet one hears it said, "anybody knows what we mean!" Do they? I have found students in a number of the states of the union who are misled by such statements. Or one is told, "why worry, the dumb don't care, and the bright boys will ferret out the truth, now or later." Is that careful teaching? I trust that you will all agree that we owe the dumb boys just as much as we do the bright ones.

The major purpose of that grand teaching tool, qualitative analysis, is its use in teaching chemistry first, and separations as an incident thereto. A great many of the students who have come through courses where such misleading symbolism has been substituted for an understanding of actual ionic situations continue to contribute to the belief that technological processes involving chemical change are destined always to remain empirical, if not mystic in character. The literature of chemical technology is full of statements that illustrate this point. The ways in which we write formulas and equations are bound to influence our thinking processes. We might well strive to write that which will represent the dominant species present when the action takes place.

During the current century there has come into being a tremendous body of factual information that has thrown much light on the whole problem of molecular complexities and structures. This knowledge is continuing to grow at an accelerated rate. Those of us who have specialized in inorganic chemistry have been

very slow to use the results of studies in X-ray crystallography. Those of us who teach have been even slower. Yet here one finds many answers to the questions so clearly posed by the reservations in Professor Cooke's "old" text.

Let us choose a few simple cases. Reference has already been made to the case of the particles present in solid sodium chloride. The simplest formula for the substance has long been written to represent it. To this I have no objection. It is, however, unfortunate not to find some way by which in words or symbols we may indicate clearly that, while we have but *one* substance, we have *two* species of particles. Teachers of chemistry have long stressed this point regarding water solutions and reactions of such substances. We can now stress it for the solid state as well.

We now have a great deal of reliable information regarding the nature and complexity of ions and molecules. The evidence has been accumulated from many sources and by many methods. We might well make more use of this knowledge to illuminate our discussions. For example, the differences in chemical reactivity between anhydrous and hydrated aluminum chloride and ferric chloride come into focus when the proper formulas are written: Al_2Cl_6 and $Al(H_2O)_6^{+3}Cl_3^-$, Fe_2Cl_6 and $Fe(H_2O)_6^{+3}Cl_3^-$. The bondings thought to be involved illustrate in a very elegant fashion much of modern valence-bond theory (at least of one school of valence-bond theory). The interesting shifts between quadricovalency and sexicovalency may also serve to stimulate student understanding of such relationships. All of this might be lost if we followed the traditional pattern of writing the simplest formulas: $AlCl_3$ and $FeCl_3$.

When one writes the formula for "auric chloride" as $AuCl_3$ and then adds: "The solution must be stabilized by adding hydrochloric acid," one is encouraging a belief in alchemy. The facts about the chloraurate ion have been known for more than 50 years. Related to this is, of course, the realistic treatment of the action of aqua regia which has come to be standard in our teaching but does not seem to have been generally understood by many technologists. A belief in alchemy dies hard! I have known able metallurgical engineers who thought of "cyanidation" as being based on very complex actions and on very mysterious chemical principles. As you know, the confusion is only as regards the complexities of the ionic species. Despite these, the principle is a very elementary one and one that is readily understood.

As teachers, we shall continue to seek out simple and effective illustrations of general principles. To these we shall continue to bring the knowledge now available regarding complexities. Finally, we must choose the methods of representation that will emphasize most clearly the ideas involved.

I was asked recently to write a very brief but definitive article regarding "salts." What would you have written? Sodium chloride is a salt. Is arsenic trichloride a salt? It is not usually considered to be one. Is anhydrous aluminum chloride a salt? Is sodium peroxide a salt? They are usually not considered as such. However, one might conceivably agree that the latter is a salt that conceivably could be formed by the action of sodium hydroxide, a base, with hydrogen peroxide, an acid. It has even been argued that oxides of metals are salts, *i. e.*, conceivably formed because of the acidic character of water. It has even been argued (in a court of law) that selenium dioxide is a salt! I was forced to the statement: "Common salt, sodium chloride, can be considered to be derived from the complete interaction of sodium hydroxide with hydrochloric acid. . . . It has come to be usual to designate as salts all compounds that can be reasonably considered as having been derived in a similar fashion."

It will be noted that this statement stresses "reasonably." Certainly arsenic trichloride is excluded. It is my opinion that all oxides and peroxides are excluded both on the count of reasonableness and of customary usage. There are those who would dispute this. How do you handle this in your classes?

Modern methods of X-ray crystal study may also be called upon when compounds, whose empirical formulas might lead one to call the substances salts of oxyacids, have been shown to be instead "multiple oxides." Thus perovskite and pseudobrookite, ($CaTiO_3$, Fe_2TiO_5) cannot properly be called salts, since there are no discrete titanate ions.

In similar fashion, modern information has enabled us to differentiate clearly between true "double salts" like alums, and "complex salts" like ferrocyanides or ferricyanides. Here the facts are so well known that one seldom, if ever, sees the old and misleading formulas $4KCN \cdot Fe(CN)_2$ and $3KCN \cdot Fe(CN)_3$. However, one does sometimes find the formula for a chloraurate rendered as $KCl \cdot AuCl_3$.

It seems to me that, as teachers of chemistry, we should lead in promoting better and more precise naming of inorganic substances. During the last 20 years workers in the field have gone over almost without exception to the Stock system of naming. It has been accepted as desirable practice by the board of editors of *Inorganic Synthesis*. The more recent reference compendia indicate Stock names as alternative ones for nearly all inorganic compounds. Yet only a few authors of textbooks of general chemistry, as far as I know, have been brave enough to include even a reference to this very simple and convenient nomenclature.

Where individual teachers have used the scheme, students have found it simple and readily understandable. As teachers, we should lead, not follow! We stress the values of precise measurement; why do we lag with respect to precision in naming?

We might well also break a lance or two against another windmill—the "jargon" of the industrial chemist. To him, "nitrating" means a very different process than that indicated by "phosphating." There is even greater uncertainty as to what is meant by "sulfating," or even by "sulfonating."

One finds highly placed technologists forced to resort to empirical statements because they have taken written equations as proof of molecular situations. These errors are in effect our errors; to remedy them for the next generation is our task.

Our colleagues in the field of organic chemistry are now deeply concerned about the current jargon word "petrochemicals." I realize fully that any language is in the custody of its users and that the teachers of chemistry cannot establish correct usage by fiat. However, we should use our privileged position as a chance to give current usage a nudge. To my mind, it is our responsibility as well as our privilege.

In summary, the concepts of modern inorganic chemistry can well be used to light up the instruction in the first course in chemistry. We find, as we do so, that our students find our science both simpler and more fascinating with much less need to be "unlearned."

I must end by again stressing my unwillingness to serve either as one whose word is to be considered final or as one who knows all the answers. I can only claim to have spent 40 years making mistakes in teaching and having a fine time trying to avoid repeating them. I owe a great debt to all my former students and associates who have been so willing to accept my good intentions in lieu of better performance.

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To the Editor:

The very interesting report of "Group A" on "Reducing duplication in high-school and first-year college chemistry" (THIS JOURNAL, **32,** 141 (1955)) moves me to comment on the general subject. Roughly half of the nearly 2000 students in my first-year college chemistry classes over the past six years had had high-school chemistry and the other half had not. Of the first group, some had had an excellent course and others had not. All have taken the same college course. I have been especially interested in the problems involved in presenting to the combined groups a course which ought at the same time to be stimulating and challenging to the best prepared students and slow and simple enough for the least well prepared students. Tentatively, at least, I have concluded that fundamentally, these problems do not originate with the presence or absence or nature of a high-school chemistry background. Actually they seem not very different from problems inherent in simultaneous instruction of any group of students ranging widely in interest and ability.

My first comment is this. Although a good high-school chemistry course does make college chemistry easier, I honestly believe that any student would be much better prepared for college chemistry if instead of high-school chemistry he could acquire greater ability in mathematics, reading, and writing. It is most discouraging to have students bored with some of the most interesting parts of chemistry because it is old stuff, yet unable to do well in the course because of pitiful inexperience in arithmetic and algebra, and inability to read and write adequately.

My second comment is just a suggestion that perhaps high-school chemistry ought to be directed primarily toward those who will never take college chemistry. Accordingly, a broad survey would seem much more useful than a preview of the first course in college chemistry. The real fundamentals of chemistry are not simple, and are unlikely to be learned well at the high-school level. On the other hand, in a very qualitative, descriptive course, even omitting formulas and equations or barely mentioning them, one could give a fascinating picture of modern chemistry. Such a picture would give everyone a greater appreciation of his environment and of the role of chemistry in his daily life. It would provide a useful, although nonessential background for college chemistry without serious duplication. I believe that it would increase the number of students entering college with a positive interest in the profession of chemistry. Last but not least, such a course could be taught effectively by high-school teachers lacking thorough technical training.

R. T. SANDERSON

STATE UNIVERSITY OF IOWA
IOWA CITY, IOWA

To the Editor:

In a recent letter (THIS JOURNAL, **32**, 52 (1955)) J. P. Phillips mentions that leading texts of quantitative analysis use widely differing values for the solubility products of silver chromate and silver chloride. D. D. DeFord in the article (THIS JOURNAL, **31**, 460 (1954)) referred to by Phillips points out some reasons for the inaccuracies in equilibrium data.

One of the important reasons for the variations is that solubility products and other classical equilibrium

"constants" are not true constants at all, but vary with the electrical environment or ionic strength of the solution. DeFord pointed this out and published a graph of the variation in activities of different charge-type ions with ionic strengths. Particle size also affects solubility (see HULETT, G. A., *Z. physik. Chem.*, **37**, 385 (1901); DUNDON, M. L., AND E. MACK, *J. Am. Chem. Soc.*, **45**, 2479 (1923).

The present writer has pointed out (THIS JOURNAL, **26**, 280 (1949)) how ionic strength may be used in obtaining more nearly experimental values in calculations involving solubility products. In at least one text ("Quantitative Analysis," by RIEMAN, NEUSS, and NAIMAN, 3rd ed., McGraw-Hill Book Co., Inc., **1951**) the use of activities and ionic strengths is consistent throughout, in all calculations involving ionic equilibria. The problem on the amount of chromate to use in a Mohr titration is worked out on pages 81–4 and nearly experimental values are obtained.

The concepts of activities, ionic strength, and activity coefficients have been well known and accepted since G. N. Lewis and Debye and Hückel elucidated them in 1923. In fact Stieglitz, in his classic text "The Elements of Qualitative Chemical Analysis" (The Century Co., **1911**, Vol. 1) strongly suggests these concepts, based on his own work and that of A. A. Noyes and others.

Why is it that instructors in quantitative analysis are so reluctant to accept and teach these "new" ideas? It is certainly not true that these concepts are too difficult for the students to grasp. The writer has found, in teaching at two different institutions, that the students readily accepted the notion of interionic attraction, and used activity coefficients, activities, and variable equilibrium values as easily as they formerly did per cent ionization, molar concentration, and classical constants. It seems reasonable to introduce these newer ideas in quantitative analysis where their practical use can be illustrated, as in the case of the Mohr titration. The students are then better prepared to deal with the derivation and use of the Debye-Hückel equation when encountered in physical chemistry.

It appears possible that the instructors are more fearful of accepting new concepts than are the students.

BARNET NAIMAN

THE CITY COLLEGE
NEW YORK, N. Y.

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● NON-AQUEOUS TITRATION

Santi R. Palit, Mihir Nath Das,* and *R. R. Somatajulu. **Indian Association for the Cultivation of Science, Calcutta, 1954. viii + 122 pp. 23 figs. 2 tables. 14 × 20 cm. $1.**

THIS concise summary of titrimetric procedures in nonaqueous media is primarily concerned, of course, with "acid-base" methods. But in the broadened sense with which this term is applied to nonaqueous systems, quite a variety of inorganic and organic determinations are included.

Both potentiometric and chemical indicator techniques are widely used for end-point detection. Most of what has been described in the literature is reviewed. The descriptions are necessarily brief and do not give fine points of experimental detail. But the principal precautions to be observed, the precision and accuracy of a given technique, and any notable advantages or limitations are often mentioned.

A brief general background and summary of acid-base theory occupies the first 22 pages. Five chapters totaling 54 pages comprise the major portion of the book, which is concerned with the various classes of determinations that can be made in glycols as solvents. One of the authors (Palit) has played a major role in the initial development of titrimetry in glycolic solvents. A 20-page section reviews the work that has done been in glacial acetic acid, and 12 pages are devoted to determinations of weak acids in a variety of solvents.

About 250 references are cited which is indicative of a reasonably complete coverage for this relatively new and specialized field. There are 23 figures and several tables. The typography is clean and the binding is adequate. The authors' tendency toward occasional cumbersome sentences and awkward choices of words is more than compensated by the availability of 130 pages of cloth-bound book in English at only one dollar.

CHARLES L. RULFS

UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

● NAME REACTIONS IN ORGANIC CHEMISTRY

Alexander R. Surrey. **Academic Press, Inc., New York, 1954. viii + 192 pp. 15.5 × 23.5 cm. $4.**

ONE or two pages of this small volume are devoted to each of 113 "name reactions" in organic chemistry. A short biographical sketch of each "name" author is given. This is followed by

a brief description of the reaction conditions and an over-all general equation. An example of the synthetic usefulness of the reaction is generally given, together with one or more leading references to recent work. A statement regarding pertinent information relative to the mechanism of the reaction is often given together with illustrative equations.

The book is well and attractively written. It will serve as a convenient first reference for the practicing organic chemist, and should be of benefit to graduate students who wish to survey a variety of reactions.

It is questionable in the mind of the reviewer whether the use of names to identify a reaction should be further encouraged, particularly to the extent of including such less familiar examples as the Béchamp reduction, the Combes quinoline synthesis, the Duff reaction, the Pictet-Spengler reaction, and the Pomeranz-Fritsch reaction.

The author has deviated somewhat from his usual selection of well known reactions by including about 17 related to quinoline chemistry. The compilation of biographical sketches of more than 100 organic chemists is not one of the lesser contributions of this work.

F. G. BORDWELL

NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

● LABORATORY PRACTICE OF ORGANIC CHEMISTRY

G. Ross Robertson, **Professor of Chemistry, University of California, Los Angeles. Third edition. The Macmillan Company, New York, 1954. x + 377 pp. 14 × 21 cm. $4.**

THIS laboratory manual is extremely flexible and comprehensive. There is adequate material to satisfy the most avid student of elementary organic chemistry. Also, this manual should meet the requirements of the most fastidious teacher. Undoubtedly this manual could be used as the nucleus of an advanced course in synthetic organic chemistry because directions are given for and reference is made to many specific type syntheses and to the more fertile sources of organic syntheses in the chemical literature.

Part I (Theory and General Technique), which occupies nearly one-half of the book, contains several quite adequate, elementary treatments of the fundamental physical principles involved in the manipulations of organic liquids and solids, either as pure substances or in mixtures. The techniques used in the various types of distillation are discussed exceptionally well. The author rightly maintains that the procedures used in the common manipulations of organic compounds are based on important physical principles, and that the organic laboratory offers an exceptional opportunity in which to illustrate these principles, especially to those students who do not take a formal course in physical chemistry. The experiments which illustrate these principles are included with the preparative experiments in Part II (Laboratory Experiments).

Part II of this third edition has been revised rather extensively. More experiments of the "general introductory" type have been added, apparently at the suggestion of teachers who used the previous edition. Several preparative experiments have been added, and a few experiments have been deleted. For example, the preparation of ethanol by fermentation has been added, and the experiment on the inversion of sucrose has been deleted. Experimental directions have been simplified in certain synthetic experiments, such as in the preparation of propylene dibromide.

The most unique "experiment" in this edition is the "Library Problem." The author suggests that a written term report be assigned to the student about half way through the year's work in organic laboratory. It is suggested that this report be a reasonably thorough, scholarly discourse based on literature references to the synthesis, structure, and properties of an organic compound,"—not an extremely rare substance, and yet not a common compound." The author proposes a reasonable plan of procedure, but of course this commendable pedagogical device could be used quite flexibly. In any event, such a literature search should be a productive stimulus, especially for the more able students.

Other notable features in this manual are the wide selection of instructive experiments, the thoughtful questions and problems which follow most chapters in Part I, the many experiments in Part II, the long list of special experiments and synthetic sequences, and the abridged section on organic qualitative analysis.

Perhaps some students may be somewhat confused by an occasional cumbersome sentence, but for the most part this manual is clear and concise. Most students and teachers should find this book an extremely useful supplement to a formal textbook of organic chemistry.

DONALD C. GREGG

UNIVERSITY OF VERMONT
BURLINGTON, VERMONT

● THE NEW ATOMIC ENERGY LAW: WHAT IT MEANS TO INDUSTRY

Atomic Industrial Forum, Inc., New York, 1954. vi + 181 pp. 21.5 × 27.5 cm. Paper bound. $5.

WHEN a structure of legal regulation has to be built far ahead of the activities it is supposed to control, it is bound to be the subject of much debate. Such a law is the Atomic Energy Act of 1954. If the participants in the debate are individuals best qualified by experience, training, and point of view, the record of their discussions is a comprehensive, authoritative document. Such a document is this printed transcript of the proceedings of a meeting for members and guests of the Atomic Industrial Forum, Inc., in September, 1954. The list of topics includes almost every facet of the tremendously complicated problem of making peacetime nuclear energy a part of the nation's economy. The list of contributors reads like a "Who's Who" of science, industry, law, and government. There is an interesting optimistic nuance to all their discussion: They are addressing themselves to the problem of how to do the job, not whether it can be done. The material is on a technical level intelligible to economist and scientist. It is the only report now available on this very timely subject.

WILLIAM F. KIEFFER

COLLEGE OF WOOSTER
WOOSTER, OHIO

● CONDENSED PYRIDAZINE AND PYRAZINE RINGS (CINNOLINES, PHTHALAZINES, AND QUINOXALINES)

J. C. E. Simpson, **late member scientific staff, Medical Research Council, England. Interscience Publishers, Inc., New York, 1953. xvi + 394 pp. 16 × 23.5 cm. $12.50. Subscription price, $11.25.**

THIS volume is the fifth in the series "The Chemistry of Heterocyclic Compounds." It actually consists of three separate monographs: a short but complete presentation of cinnoline chemistry; a longer and equally exhaustive review of phthalazines; and a less complete summary of the field of quinoxaline chemistry which was already well developed when the heterocyclic volume of Meyer-Jacobson's "Lehrbuch der organischen Chemie" appeared 35 years ago. The quinoxaline portion of the present volume may be considered as an extension of the earlier review, although there are numerous references to the literature prior to 1920 and the text is readily understood without reference to other material. There are also three very useful, brief appendixes covering ultraviolet absorption spectra, basic strengths, and physiological activities of compounds of these classes. More highly condensed heterocyclic systems containing an intact cinnoline, phthalazine, or quinoxaline nucleus are included in this work as well as aza derivatives in which one CH group of these nuclei is replaced by N; compounds in which the replacement is by another hetero atom

are excluded, as are phenazines, condensed phenazines, and their aza analogues. The treatment of each class of compounds is systematic, separate chapters being devoted within each major portion of the book to compounds containing each functional group or type of group. A carefully compiled table accompanies each chapter, enabling one to find any given compound with ease.

Dr. J. C. E. Simpson was an authority in the field of heterocyclic chemistry and made many original contributions, especially in the field of cinnolines. His excellent book is indispensable to anyone working with the types of compound covered and should be available for reference not only to organic chemists in the heterocyclic field, but to many others as well.

THOMAS L. JACOBS

UNIVERSITY OF CALIFORNIA
LOS ANGELES, CALIFORNIA

● QUALITATIVE SCHNELLANALYSE NACH G. CHARLOT

Edited by A. Schleicher. Walter de Gruyter & Co., Berlin, 1954. vi + 82 pp. 13.5 × 19 cm. Paper bound. DM 7.80.

THIS book is comprised of a 60-page translation of G. Charlot, D. Bézier, and R. Gauguin, "Analyse Qualitative Rapide des Cations," Paris, 1950 (this portion has also been translated into English by Oesper as "Rapid Detection of Cations," Chem. Publishing Co., 1954); and a 20-page section on the anions, based on an article by J. M. Odekerken in *Z. anal. Chem.*, **131**, 165 (1950).

Charlot, *et al.*, describe tests for about 38 metallic ions, and a feature of the book is that these embrace many "less familiar" elements such as Tl, U, Ga, Re, Ce, Th, Be, Mo, W, V, Ti, and Zr. The scale of work described is semimicro, and a minimum of apparatus is employed.

The cation procedure involves no systematic group separations beyond the initial removal of silver and mercurous halides, silica, complexing anions, etc.; but certain preliminary tests are recommended. These include tests with ammonia in which the colors of supernatant and/or precipitate are observed. Sodium sulfide is added to the same system and any color changes resulting from the conversion to sulfides are noted. An exploratory test with cupferron in 1.5 *N* hydrochloric acid is especially pertinent when such elements as Zr, Mo, Ga, V, Ti, etc., may be present.

One or more good confirmatory test is given for each cation in terms of concise statements on the nature of the reaction, the reagents, procedure, sensitivity, interferences, and miscellaneous remarks. A very judicious selection of the most selective, reasonably sensitive, and reliable test has been made in most instances. Useful inorganic or classical techniques are never displaced by high-sensitivity, but low-selectivity, organic reagents. But useful organic reagents like dimethylglyoxime, aluminon, cupferron, alpha-benzoinoxime, ortho-phenanthroline, etc., are freely used wherever they present a real advantage. The authors' discrimination in this crucial matter is usually above reproach.

Odekerken's material on the anions includes about 24 species; many of the metals characterized in the previous section could be classed as anions, of course. To the usual preliminary anion-group tests with silver nitrate and barium chloride are added useful tests for oxidizing or reducing substances. Iodide is used to test for oxidants and iodine for reductants. Permanganate is also used to check for weaker reducing agents. Again, the individual confirmatory tests are not novel but are usually well chosen.

The typography is good and there seem to be relatively few errors of fact, though the erroneous ascription of the rhenium (IV) thiocyanate color to perrhenate (VII) ion was noted.

Some of the pedagogical advantages claimed by Charlot for his nonseparation scheme may not find wide agreement in this country. But viewed as a practical approach to finding out what is in an unknown material with a minimum of time and fuss, the Charlot approach is excellent.

CHARLES L. RULFS

UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

● GLUTATHIONE

Proceedings of the Symposium held at Ridgefield, Connecticut, November, 1953. Edited by *S. Colowick, A. Lazarow, E. Racker, D. R. Schwarz, E. Stadtman,* and *H. Waelsch.* Academic Press, Inc., New York, 1954. x + 341 pp. 62 figs. Tables. 15 × 23.5 cm. $7.50.

GLUTATHIONE was first prepared from yeast in crystalline condition by F. G. Hopkins in 1921 and its structure was determined a few years later. The widespread occurrence of this tripeptide in animal and plant cells, its unique structure, and ease of oxidation suggested an important physiological role for it. The early workers concluded that glutathione could not function as a hydrogen carrier for the bulk of tissue oxidations and that its function in oxidation and reduction was more specialized. To find the exact significance of glutathione has been the subject of intensive research since its discovery. This symposium reviews the current thinking with respect to this interesting substance.

The many experimental approaches to this problem that have been made in recent years are indicated by the variety of topics discussed at this symposium. Twenty-nine papers were presented under the following main headings: (1) Properties and Organic Chemistry, which include mercaptans and disulfides, thiol-thiolester formation, as well as the chemistry of glutathione; (2) The Methods for Detection and Assay of Glutathione and Sulfhydryl Compounds, in which paper chromatography, histochemical experiments, and the classical methods are described; (3) Biochemical Mechanisms. In this part, enzymatic oxidation, biosynthesis of glutathione, transpeptidation reactions, glutamyl transfer, glutathione as a coenzyme, and SH and growth are included; (4) Physiological Actions and Clinical Aspects. The relation of glutathione to hormone action and diabetes, glutathione in radiation injury, and glutathione in human disease are among the topics discussed. Fifty-seven individuals are listed as contributors to the symposium.

The value of this book rests on the bringing together in one volume of the observations and ideas that have accumulated over the years from many areas of biological science. The subject of sulfhydryl chemistry is one of great interest to many investigators and our knowledge of glutathione and its functions undoubtedly will expand. This book, valuable as it is today, will then begin to be of historical interest only. It would be a great service to scientific readers if publishers of symposia of this nature would appreciate the transient character of such progress reports and manufacture a book that could be reasonably priced. The reader's investment then would be commensurate with its probable use.

F. A. CAJORI

UNIVERSITY OF COLORADO
DENVER, COLORADO

● CHEMICAL THERMODYNAMICS

I. *Prigogine* and *R. Defay*, Professors in the Université Libre de Bruxelles. Translated by *D. H. Everett*, University of Bristol. Longmans, Green and Co., New York, 1954. xxxii + 543 pp. 152 figs. 40 tables. 15.5 × 24 cm. $12.50.

TO QUOTE from the Introduction: "This book is the first volume of a "Treatise on Thermodynamics" based on the methods of Gibbs and de Donder. It deals with the following topics: fundamental theorems, homogeneous systems, heterogeneous systems, stability and moderation, equilibrium displacements and equilibrium transformations, solutions, azeotropy, and indifferent states. The second volume deals with surface tension and adsorption while the third and last will be concerned with irreversible phenomena."

This volume covers the preceding list of topics in 29 chapters and a preliminary discussion on notation (including a long list of symbols) of 11 pages.

De Donder and his "Brussels school" have developed a new for-

mulation of thermodynamics, which treats irreversible phenomena and the production of entropy with the aid of two new functions, the *affinity* and the *extent of reaction*. A listing of a few of the topics in the first five chapters may give a hint as to how the authors of this book present these ideas:

Rate of reaction; Generalized definition of extent of reaction; Entropy changes and entropy creation; Production of entropy and rate of reaction; Significance of the affinity; Statistical interpretation of the production of entropy; Affinity and heat of reaction; Affinity as a function of temperature; Affinity and thermodynamic potentials; Total differential of the affinity; Average values of the heat of reaction; Average values of the affinity; Relations between the heat of reaction and the average affinity.

After the exposition of the new ideas of de Donder, the authors proceed "...to deal not only with the more elementary applications, which are in fact the only ones which are treated in most recent textbooks of thermodynamics, but also those requiring a much more elaborate development."

From this quotation from the Introduction one may readily understand that the book is not intended to be used as a textbook in a first course in thermodynamics.

W. F. LUDER

NORTHEASTERN UNIVERSITY
BOSTON, MASSACHUSETTS

● ION TRANSPORT ACROSS MEMBRANES

Edited by *Hans T. Clarke* and *David Nachmansohn*. Academic Press, Inc., New York, 1954. xi + 293 pp. Figs. and tables. 16 × 23.5 cm. $7.50.

THIS book is a collection of papers presented at a symposium held at the College of Physicians and Surgeons, Columbia University, in October, 1953. Such a collection of papers generally makes for a rather incoherent monograph and this book is no exception, since the extent to which the editors can perform their editorial function is somewhat limited in dealing with 20 or more contributors. Although most of the individual papers are in themselves coherent, there is little attempt made to correlate the ideas of the individual authors into a single pattern, and the reader must attempt to do this for himself.

A very brief introduction by W. J. V. Osterhout describes the investigations of Loeb which brought out clearly the need for a better understanding of membrane phenomena, and particularly of the problems involved in the transfer of materials across membranes.

A paper by Hans H. Ussing describes the techniques which may be used to measure permeabilities of animal membranes and for the simultaneous measurement of ion transport and current drawn during short circuit of the membrane, *i. e.*, under conditions in which the opposite sides of the membrane are connected by very low-resistance electrodes. From the results of such experiments one can derive considerable insight into the migration of ions across the membrane since the short-circuit is caused by the migration of charged species.

A. F. Huxley discusses the effect of membrane potential on the permeability to various ions of biological nerve membranes like that of the giant squid. The effect of applied potential across the membrane greatly changes the permeability of such a membrane as compared to that in its resting state, and it appears that quite separate membrane mechanisms are involved in the transport of ions as closely related as sodium and potassium.

An interesting paper by I. B. Wilson and D. Nachmansohn attempts to answer the question of what biological processes are involved in the marked changes in permeability of membranes under electrical polarization as discussed by Huxley. These authors present strong arguments for belief that acetylcholine-acetylcholinesterase interactions are fundamentally involved. These conclusions are substantiated by good deal of experimental work on the permeability changes of membranes. A short paper by S. L. Freiss, J. J. Blum, and M. F. Morales deals with an optical study of the cholinesterase-acetylcholine system.

A short paper by A. K. Parpart and J. F. Hoffman summarizes present knowledge relating to the permeability of the red cell, and a paper by G. H. Mudge deals with electrolyte transport in the kidney.

R. B. Parlin and H. Eyring discuss the transport of matter through membranes in terms of the now familiar activated step mechanism and apply their results to a consideration of the transport of sodium and potassium chlorides through a model nerve-cell membrane. A paper by J. G. Kirkwood applies the ideas of nonequilibrium thermodynamics to the transport of ions, and a paper by G. Scatchard deals with the thermodynamics of ion-exchange membranes.

K. Sollner, S. Dray, E. Grim, and R. Neihof deal at length with the properties of a number of model membranes which permit a useful test of postulated mechanisms for membrane transport, in that the membranes, mostly developed by Sollner, can be charged; this paper brings out very clearly the limitations of some earlier views relating to the acquisition of charge by artificial membranes such as collodion, gelatin, etc., as well as giving a critical view of the part actually played in real biological systems by so-called anomalous osmosis. This paper also discusses the behavior of selectively permeable membranes and their possible applications in preparative chemistry.

A paper by T. L. Hill discusses the subject of protein solutions rather ambitiously in terms of the statistical theory of McMillan and Mayer. It is doubtful whether many biologists, or even many physical chemists possess the background necessary for a complete understanding of this highly condensed paper, which is marked not only by complicated typographical notation but also by frequent parenthetical remarks which make it hard to read.

The interaction of metal ions and proteins, which is clearly important in any interpretation of transport across biological membranes, is dealt with in a paper by J. T. Edsall and in one by F. R. N. Gurd. These papers present the results of detailed experimental work at Harvard on the interactions of metals with serum albumins, and the point is clearly made that, for example, zinc ions and lead ions interact at very different sites. This kind of evidence lends support to the notions of separate ion-transport mechanisms for different ions, as discussed earlier by Huxley.

A paper by P. Debye on the influence of rather large electric potential gradient on the sedimentation of uncharged particles deals, in a way which is characteristically simple and elegant in Debye's work, with the effect which electric field strength exerts on molecules which can develop induced dipoles. From simple premises Debye shows how the sedimentation equilibrium under strong electrical fields can be used to determine the molecular weight of polymers in terms of the change in capacity which occurs in a condenser owing to the migration of polymer. What is of interest here, from the viewpoint of ion transport, is that the high potential gradients involved in these experiments are of just that order of magnitude encountered in the vicinity of small ions, so that the movement of even uncharged molecules in the pores of a charged porous membrane has to be considered in any complete theory of membrane transport.

This collection of papers brings together the views of some of the leading physical biochemists and physical chemists of our time, and anyone interested in the detailed mechanisms of membrane transport could scarcely fail to be stimulated by reading these papers. The book, however, does not constitute a textbook on the subject of membrane transport suitable for the bookshelves of most teachers.

The printing, binding, and format of the book are very good, and the price is reasonable for a book of this kind.

ERIC HUTCHINSON

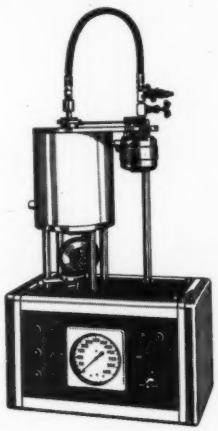
STANFORD UNIVERSITY
STANFORD, CALIFORNIA

⊙ ⊙ ⊙

Out of the Editor's Basket

Rheometers

Castor-Severs Extrusion Rheometers are offered by Burrell Corporation for the measurement of viscosity at high rates of flow in control, formulation, research, and production processes.



The new line of rheometers are complete unit-package instruments delivered ready for use as reliable tools for the accurate measurement of viscosity of coatings, adhesives, pastes, and plastisols in the fields of petroleum, paint, inks, resins, foods, chemicals, and wherever else thickness of material may be a factor.

Request information on Castor-Severs Extrusion Rheometers, Burrell Corporation, manufacturers and distributors of scientific apparatus and laboratory chemicals, 2223 Fifth Ave., Pittsburgh 19, Pennsylvania.

New Spectrochemical Instrument

Applied Research Laboratories, Glendale, California, has just introduced the "Quantograph," termed by the manufacturer as a new instrumental concept in spectro-chemistry. This new instrument combines the features of a spectrograph, a monochromator, and the ARL "Quantometer," and performs the complete functions of each.

The machine is said to incorporate the advantages of three concepts in spectrochemistry: photography of spectra for complete analysis, polychromatic spectrometry for direct-reading quantitative analyses, and monochromatic spectrometry for qualitative and quantitive analyses.

Gardner Pressurized Viscosity Cup

A simple, low-cost instrument to measure the relative flow properties of heavy-bodied materials is now available along with other testing instruments from Gardner Laboratory Inc., 4723 Elm St., Bethesda 14, Maryland. Contact them for the *Gardner Newsletter* and catalogue.

Conductivity Instruments Available in 0 to One Micromho Range

Electrolytic conductivity recorders and indicators are available from Industrial Instruments, Inc., Cedar Grove, New Jersey, in the low range of 0 to one micromho. These instruments are especially useful in work with very high-quality mixed-bed demineralizer effluent. Associated equipment such as automatic temperature compensating cells is available from Industrial Instruments, Inc.

New Industrial Pycnometer

Machined from solid Plexiglas, the new weight-per-gallon cup permits the measurement of corrosive liquids which would damage metal instruments. It also provides a wide mouth for easy filling with viscous pastes and liquids. The optical clarity of the cup helps eliminate errors in measurement by allowing a visual check for bubbles. Made by the Gardner Laboratory, Inc., Bethesda, Maryland.

Laboratory Model Mill

Kinetic Dispersion Corporation announces the introduction of an improved laboratory model mill for test and pilot dispersions. In principle it is the same as the high speed, kinetic, plant scale "Kady"

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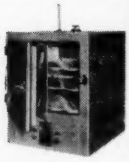

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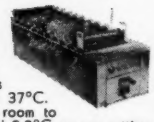

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High Temperature Saybolt Viscosimeter

A High Temperature Saybolt Viscosimeter, for determining the viscosity of asphalts, road oil, and fuel oils at test temperatures from 100° F. to 475° F., has been introduced by the Emil Greiner Co., 20–26 N. Moore St., New York 13, New York.

Bottle Pump

The Barnstead Still & Sterilizer Company announces a new bottle pump for the removal of distilled water and other liquids from carboys, tanks, etc. It is designed to protect contents at all times from contaminating matter which may enter during time of storage or when liquids are being removed. The manufacturer states that once the Barnstead Bottle Pump has been installed in the container, no air-borne bacteria, dust, mist, radioactive mist, is permitted to enter. The air which is forced into the container is automatically cleaned since it must first pass through the special Ventgard filter which removes and absorbs the various impurities before it can enter the container to replace the liquid being pumped out.

For complete information write the manufacturer, Barnstead Still & Sterilizer Co., 2 Lanesville Terrace, Forest Hills, Boston 31, Massachusetts.

Tissue Grinders

Completely interchangeable tissue grinders were recently announced by the Kontes Glass Company. The Company claims that if a pestle or tube is misplaced

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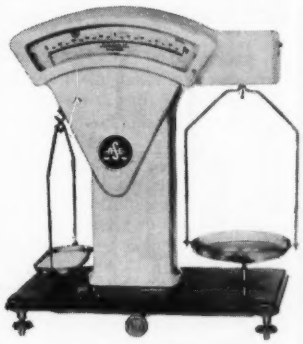

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or breaks the remaining part will fit a replacement within standard clearances (0.004″ to 0.006″). Literature on these items will be sent on request by Kontes Glass Company, 26 Spruce Street, Vineland, New Jersey.

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Measure the temperature of gases, solutions, solids quickly and accurately, from a distance. Contact Simpson Electric Co., 5200 W. Kinzie St., Chicago 44, Illinois, for further details.

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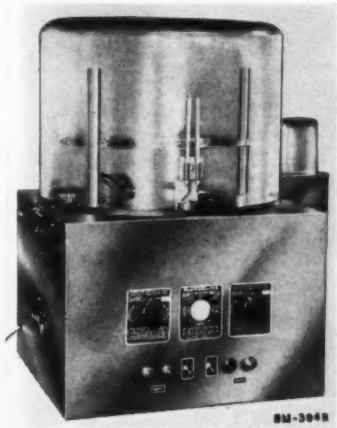
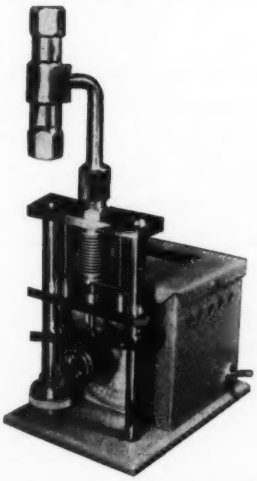


New revolutionary idea, for the first time, Blue M makes available to all research and testing laboratories a versatile and accurate low cost mechanical convection temperature controlled relative humidity cabinet, known as Vapor-Temp. Blue M Electric Co., 138th and Chatham St., Blue Island, Illinois.

Micro-Bellows Pump



Research Appliance Co., 143 Cemetery Lane, Pittsburgh 9, Pennsylvania, has available a Micro-Bellows pump with micrometer settings capable of delivering from 15 to 6000 ml. per hour by adjustment. It is small in size and weighs only 10.2 lb.

Technical Balance Has Chain Fraction Loader

The Reyers-Rapid is the first technical balance (1-kg capacity) equipped with a chain loading device that dispenses with fractional weights. Its outstanding design innovation is the attachment of two chains, one to each arm of the beam, instead of just one, so that raising the beam into weighing position does not upset its equilibrium. Arthur S. Lapine & Company, 6001 South Knox Ave., Chicago 29, Illinois.

"Nalgon" Tubing

A completely new flexible tubing, called "Nalgon" is being marketed by the Nalge Co., Inc. This tubing is characterized by its chemical resistance, flexibility, water-white transparency, and resistance to aging. Literature and samples are available from The Nalge Co., Inc., 625 South Goodman St., Rochester 2, New York.

NEW LITERATURE

● Technical information on dibutyl fumarate, a reactive resin and chemical intermediate, available in semi-commercial quantities and an extensive bibliography on its reactions can be obtained by requesting Monsanto Technical Bulletin No. ODB-54-18 from the company's Organic Chemicals Division, St. Louis 1, Missouri.

● A three-page bulletin, *Manufacturers of Molybdenum Chemicals*, has just been published by Climax Molybdenum Company, 500 Fifth Avenue, New York, to aid purchasing, production and research person-

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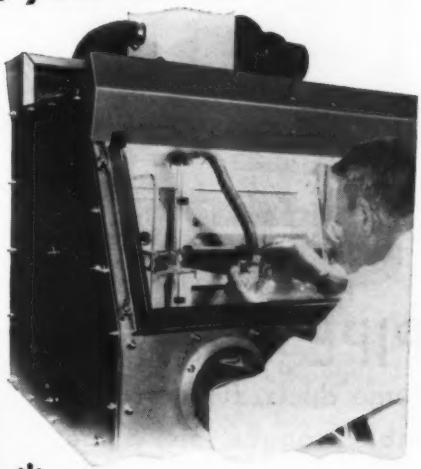
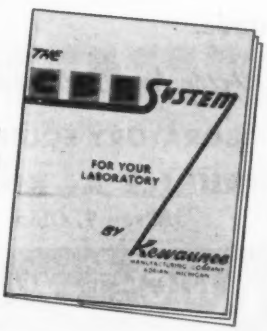


* Chemical Biological Radiological



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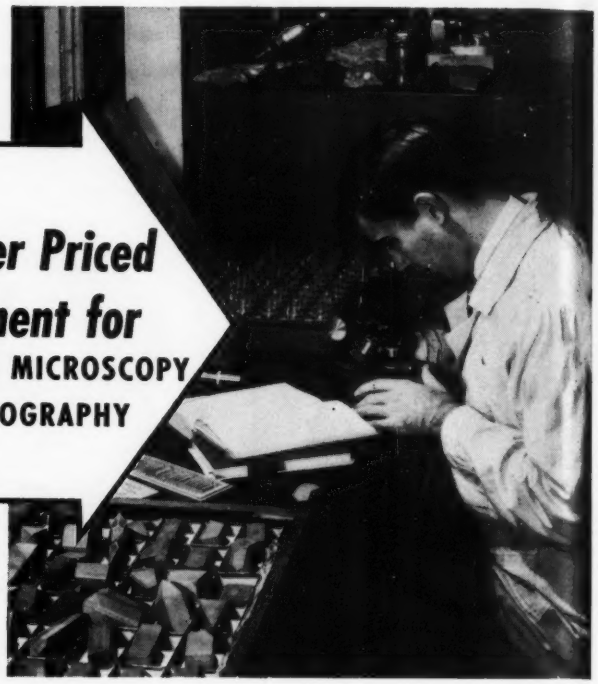

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nel in finding sources of molybdenum chemicals.

● The many ways that sodium dispersions can be used to speed chemical reactions—and make possible new reactions—are outlined in a new brochure *Using 'Ethyl' Sodium in Dispersed Form.* Copies of the booklet are available upon request from Ethyl Corporation, 100 Park Ave., New York 17, New York.

● National Bureau of Standards Miscellaneous Publication M187, *Directory of Commercial and College Laboratories,* has been withdrawn from circulation. An up-to-date revision of this publication is now available in the *Directory of Commercial and College Testing Laboratories,* recently issued by the American Society for Testing Materials. The two organizations have agreed that ASTM undertake the responsibility for compilation and publication of the Directory in the future.

The new Directory may be obtained from the American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pennsylvania, at $1.00 a copy.

● A new edition of *Mesa Miracle,* a 36-page booklet describing the fast-growing uranium industry on the Colorado Plateau, has just been published by United States Vanadium Company, a Division of Union Carbide and Carbon Corporation, Room 308, 30 East 42nd St., New York 17, New York.

● For several years past the Microcard Corporation has been producing Microcard copies of AEC reports at the Technical Information Service Headquarters at Oak Ridge, Tennessee. These reports in their Microcard form have found widespread acceptance and use in the various Atomic Energy Commission sites and laboratories. For more information write Micro Card Foundation, Middletown, Connecticut.

● A flow chart showing how molybdenum is manufactured and controlled quality-wise from oxide to finished product is featured in a new 20-page brochure issued by Sylvania Electric Products, Inc.

The booklet, *Sylvania Molybdenum,* NP-428, is available upon request from their advertising department, 1740 Broadway, New York 19, New York.

● Catalogue 5002 is a new issue of the composite catalogue which briefly and concisely describes Honeywell industrial instruments and equipment, including the latest developments. Contact Minneapolis-Honeywell Regulator Company, Industrial Division, Wayne and Windrim Avenues, Philadelphia 44, Pennsylvania.

● A handy Electrode Reference Table for users of Beckman pH meters is now available from Will Corporation, Rochester 3, New York. Listed are the sixty most widely used electrodes which Will stocks, along with descriptions; temperature and pH ranges; body and lead lengths; Beckman and Will catalogue numbers; and prices.

● A new four-page bulletin, "Properties of Molybdenum Pentachloride" is now available on request from Dept. L, Climax Molybdenum Company, 500 Fifth Avenue, New York.

Designated Bulletin Cdb-3, the publication gives the more important physical and chemical properties of chemically pure

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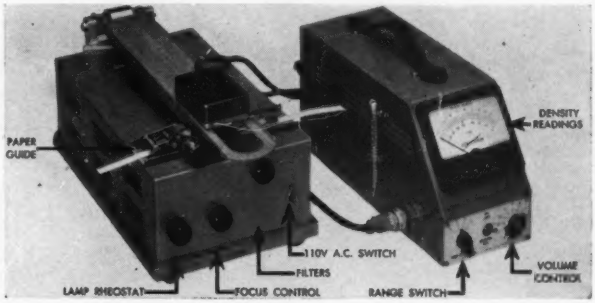

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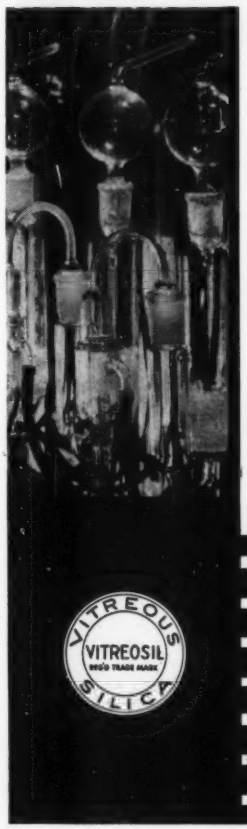

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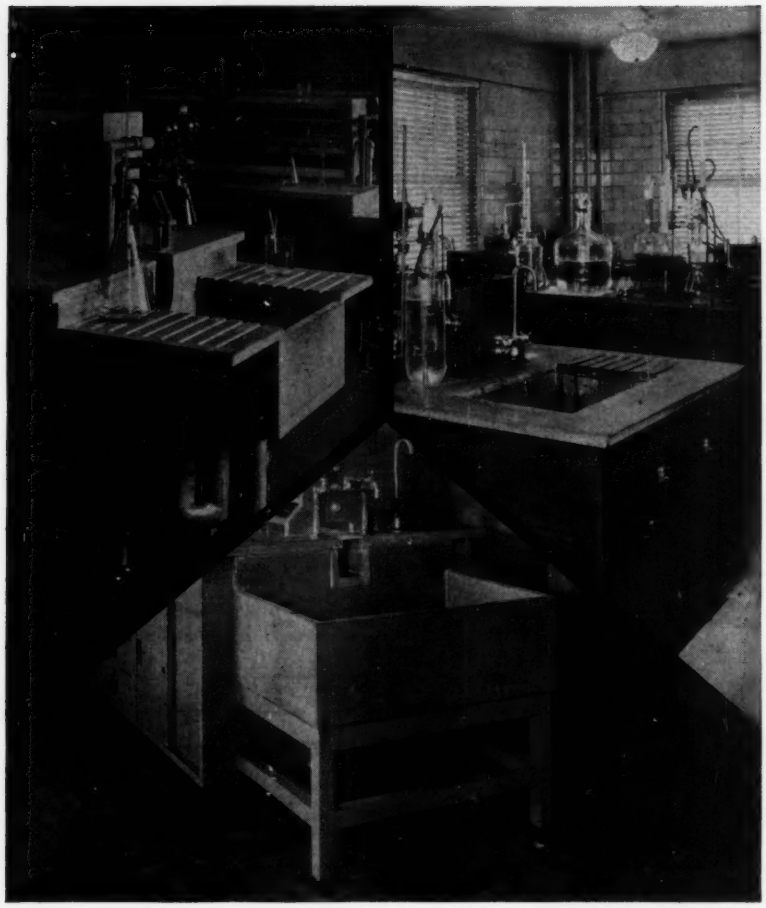

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POLAROGRAPHIC METHOD OF ANALYSIS

By OTTO H. MÜLLER, *Associate Professor of Physiology, State University of New York Medical Center at Syracuse, Syracuse, N. Y.*

In this second revised and augmented edition, the author purposes "to present a simple account of polarography in a form which can be used by teachers and students in physical chemistry as well as in advanced courses in analytical chemistry." The emphasis is on principles and the scope is descriptive rather than mathematical. It begins with an excellent review of electroanalysis, showing the relation of polarography to other electro methods. A brief description of apparatus includes equipment constructible from parts readily available in many laboratories. Fundamentals of quantitative and qualitative analysis and recent developments are discussed in some detail. Chapters on applications and suggestions for practical polarography complete the book.

A particularly good feature is the inclusion of 26 experiments, and the graphs and tables of data obtained from them constitute the illustrative material of the text. These experiments could be undertaken with profit by anyone desiring an experimental indoctrination in polarography.

The book is especially recommended to students, beginners in the field, and anyone desiring a brief but comprehensive introduction of the fundamentals of polarographic measurements.

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209 pp. *illustrated* $3.50
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CHEMICAL EDUCATION PUBLICATIONS

-------EASTON, PA.-------

molybdenum pentachloride. It also describes the preparation of the compound.

● A five-page brochure with current information describing the standard line of electronic timers manufactured by G. C. Wilson & Co., 1950–8th Avenue, Huntington, West Virginia, is now available. Included in this line are delay, repeat cycle, and interval timers all of which are available from stock.

● A four-page, two-color bulletin describing its new Diamond D Blue Line of laboratory glassware has been issued by Doerr Glass Company.

The bulletin covers in detail the features of this new laboratory glassware line: the Doerr double-test for accuracy, the electrically-controlled annealing which removes internal strain, the fusing of blue pigment in the graduations, and the care with which the line is calibrated.

Copies of this new bulletin may be obtained from Doerr Glass Company, Boulevard and Peach Streets, Vineland, New Jersey.

● A new 10-gallon jacketed pilot autoclave is illustrated and described in a new data sheet offered by The Patterson-Kelley Co., Inc., East Stroudsburg, Pennsylvania.

Besides descriptive material, the data sheet lists specifications on the jacket, top cover, agitator drive, stuffing box, and the autoclave itself.

Also included are two photographs showing front and rear views of the unit, and a large labeled line drawing.

For copies of the data sheet, contact The Patterson-Kelley Co., East Stroudsburg, Pennsylvania.

● Mann Research Laboratories, Inc., 136 Liberty Street, New York 6, New York has released a new catalog of Mann Assayed Biochemicals. Besides listing the price of individual products, specifications for each of the items are included.

With the information presented, research workers in the related fields are able to verify their starting point with reference to the individual physical and chemical characteristics.

The catalogue, with index, contains 70 pages and lists 993 items.

MISCELLANY

★ Colorlith for table tops and similar uses is a new sheet material just announced by Johns-Manville. It was developed primarily for laboratory equipment. However, Colorlith is also a suitable bench and table top material for printing plants, machine shops, institutional kitchens, and furniture for the home.

Basically a mixture of portland cement and asbestos fibers, Colorlith resists heat, impact and most types of active chemicals. It is available in two colors—charcoal gray and cameo brown.

For further information, a 4-page illustrated brochure on Colorlith is available by writing to Johns-Manville, 22 East 40th St., New York 16, New York.

★ An important new unit was added to Arnold O. Beckman, Inc., 1020 Mission St., South Pasadena, California, operations recently with the formation of a Custom Products Department headed by Mr. Robert W. Negus. Over recent years, there has appeared a growing demand for instruments and auxiliary equipment for specialized applications. Because of this demand, the Custom Products Department was created to handle work of this nature.

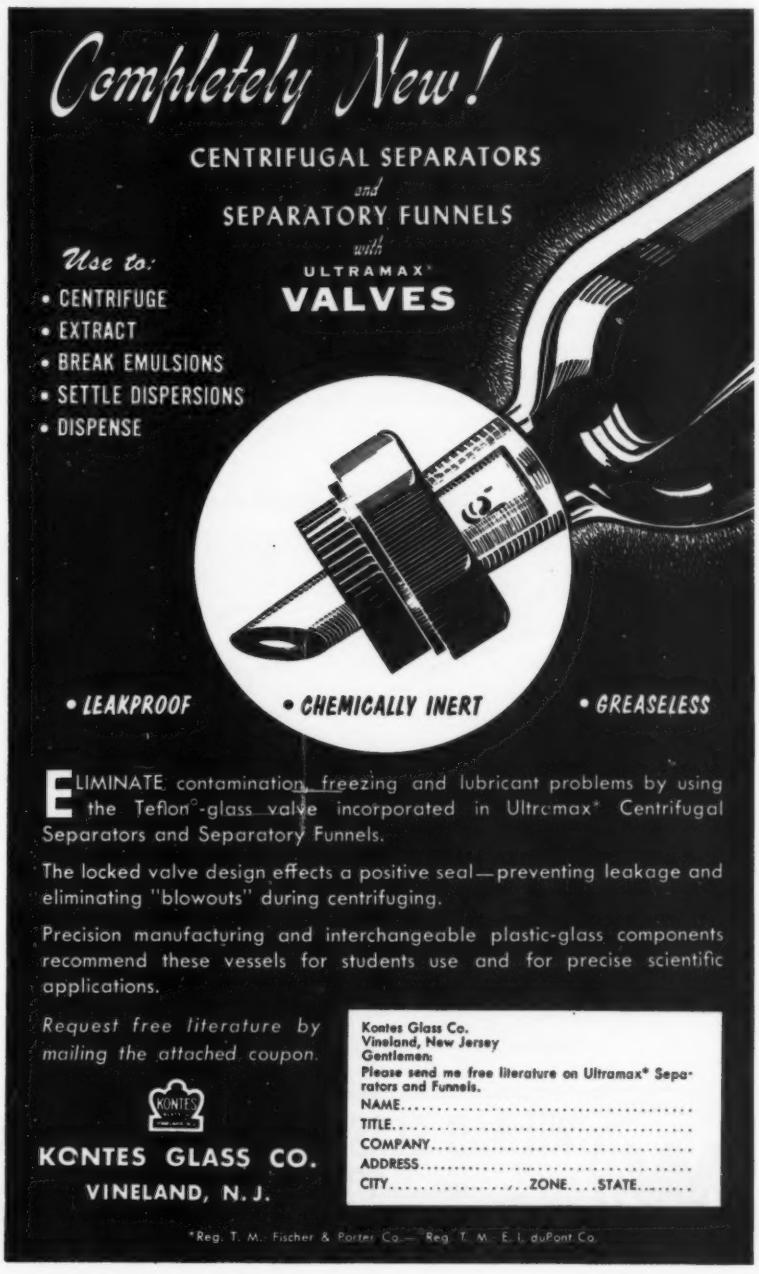
★ Atomic scientists can now see and photograph radioactive specimens in 3-D, it was disclosed today.

An unusual "periscopic, steroscopic telescope" makes this possible. It was designed and built by E. Leitz, Inc., here for the Knolls Atomic Power Laboratory, Schenectady, New York, operated by the General Electric Company for the Atomic Energy Commission. It is already in operation.

One of the first of its kind, the device permits scientists on the outside to look at "hot" materials within the cell, behind high density concrete walls three feet thick.

★ The January-February 1955 issue of *Ethyl News* has two very interesting stories for the chemist. Be sure and read S. P. Nickerson's "What's Ahead For Sodium" and Graham Edgar's "How The Octane Scale Was Created."

★ *Esso Oilways* for March 1955 tells of the great industrial transformations from "The Sands of Time," the interesting story of Fiberglas.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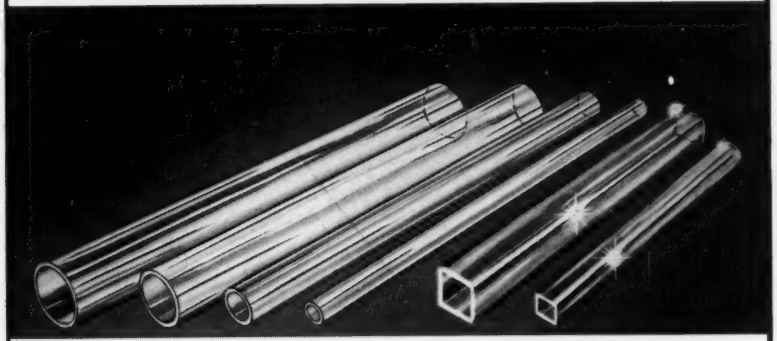

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Made in various shapes and sizes . . . square, rectangular, hexagonal, and tapered up to 7" ID. Fluted and other special shapes can be made to meet individual requirements. Available in Pyrex Brand, Vycor Brand and most of the electronic glasses.

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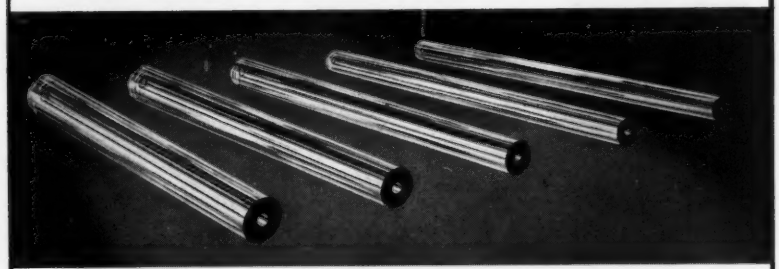

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- General Purpose, Gravity Convection, Freas, Stainless Steel finish
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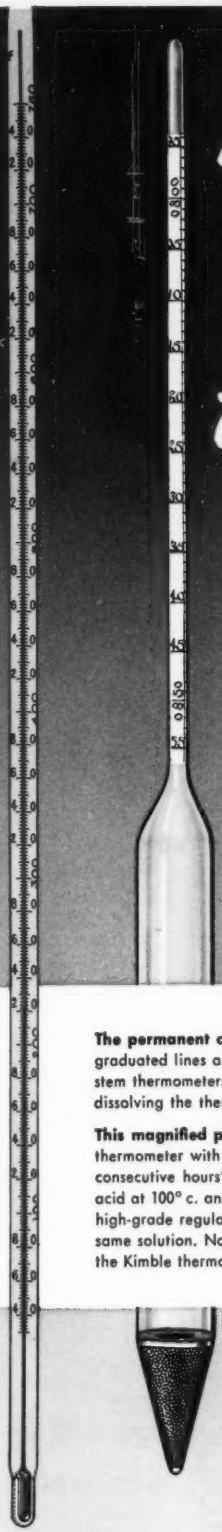
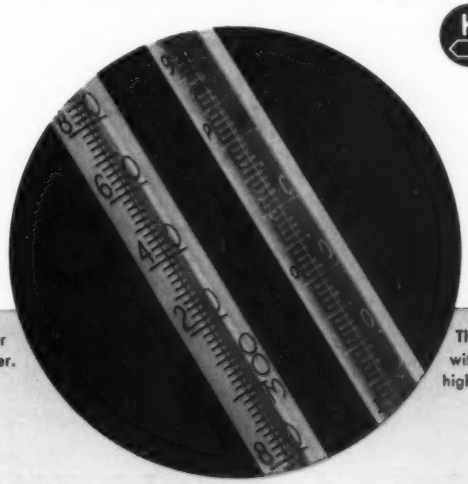
At the old price these instruments were an excellent value. At the new prices they are an even better bargain. Your laboratory supply dealer will give you complete information. Or write direct to Kimble Glass Company, subsidiary of Owens-Illinois, Toledo 1, Ohio, for illustrated price list.



The permanent colored material used to fill the graduated lines and numbers of Kimble etched stem thermometers can be removed only by dissolving the thermometer glass itself.

This magnified photograph shows a Kimble thermometer with *permanent filler* after 1500 consecutive hours' exposure in concentrated nitric acid at 100° c. and another thermometer with a high-grade regular filler after 5 minutes in the same solution. Notice how the *permanent filler* of the Kimble thermometer on the left is unaffected.



Kimble thermometer with permanent filler.

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